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(54) **AQUEOUS, SILICONE-MODIFIED ACRYLATE POLYMER EMULSION**

SILIKON MODIFIZIERTE ACRYLATPOLYMEREMULSION AUF WASSERBASIS

EMULSION A BASE AQUEUSE DE POLYMERES D'ACRYLATE MODIFIE PAR SILICONE

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(73) Proprietor: **Asahi Kasei Kabushiki Kaisha**
Osaka-shi, Osaka 530-8205 (JP)

(72) Inventors:
• **YAMAUCHI, Toyooki**
Yokohama-shi-Kanagawa 230 (JP)
• **KAMIYAMA, Yasuyuki**
Zushi-shi-Kanagawa 249 (JP)

(74) Representative: **Strehl Schübel-Hopf & Partner**
Maximilianstrasse 54
80538 München (DE)

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- **DATABASE WPI Section Ch, Week 9236 Derwent Publications Ltd., London, GB; Class A26, AN 92-295669 XP002070142 & JP 04 202 515 A (NATOCO PAINT KK)**
- **PATENT ABSTRACTS OF JAPAN vol. 009, no. 254 (C-308), 11 October 1985 & JP 60 106857 A (HEKISUTO GOUSEI KK), 12 June 1985,**
- **DATABASE WPI Section Ch, Week 9227 Derwent Publications Ltd., London, GB; Class A18, AN 92-223558 XP002070143 & JP 04 149 281 A (DAINIPPON INK & CHEM KK)**
- **PATENT ABSTRACTS OF JAPAN vol. 015, no. 512 (C-0898), 26 December 1991 & JP 03 227312 A (HOECHST GOSSEI KK), 8 October 1991,**

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Description**BACKGROUND OF THE INVENTION****5 Technical Field**

[0001] The present invention relates to an aqueous, silicone-modified acrylate polymer emulsion which is capable of forming a coating having excellent water repellency, water resistance, weatherability, dispersion characteristics of pigment; gloss retentivity, stain resistance and adhesion properties. The aqueous, silicone-modified acrylate polymer emulsion of the present invention can be advantageously used as a paint, an undercoating or finish coating material for building materials, an adhesive, a pressure-sensitive adhesive, a processing agent for papers, or a finish coating material for textile fabrics, especially as a paint, or a finish coating material for building materials.

Prior Art

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[0002] When an aqueous acrylate polymer emulsion obtained by emulsion polymerization is dried at room temperature or under heated conditions, a coating is obtained which has a relatively good durability. Therefore, the aqueous acrylate polymer emulsion has been widely used as a resin for an aqueous paint. However, when a coating, which is obtained from an acrylate polymer emulsion or from a paint comprising an acrylate polymer emulsion having a pigment incorporated therein, is exposed to outdoor conditions or ultraviolet light, not only is the luster of the coating likely to be rapidly deteriorated but also the gloss retentivity of the coating is poor.

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[0003] For solving the problems as mentioned above, it was conventionally proposed to add a silicone to an aqueous acrylate polymer emulsion to increase the resistance of a coating formed from the emulsion to ultraviolet light, oxygen, water and various types of solvents, and improve the durability of the coating. With respect to prior art documents which disclose such a technique, reference can be made to Canadian Patent No. 842947, U.S. Patent No. 3,706,697, Unexamined Japanese Patent Application Laid-Open Specification No. 3-255273 and Unexamined Japanese Patent Application Laid-Open Specification No. 6-122734. However, the emulsions disclosed in these documents have poor water resistance. The reason for this resides in that an emulsifier employed in the technique of each of the above documents does not have a reactivity with the emulsified particles of the aqueous acrylate polymer emulsion but is only adsorbed on the emulsified particles, so that it is likely that water intrudes into the emulsified particles. In European Patent No. 0 401 496, a sulfonic acid group-containing ethylenically unsaturated monomer is employed. However, in European Patent No. 0 401 496, styrene is used in a large amount which is almost the same as the amount of acrylic ester employed and, therefore, the obtained emulsion is disadvantageous in that a coating formed from the emulsion is discolored upon exposure to ultraviolet light and has poor weatherability. In U.S. Patent No. 5,214,095, an ethylenically unsaturated monomer and a hydrolyzable silane are simultaneously introduced into an emulsion polymerization system in the presence of an aqueous solvent, so that the obtained aqueous emulsion has poor dispersion stability. Even if a dispersant or emulsifier, as a stabilizing agent, is added to this aqueous emulsion, when a coating formation promotor or an inorganic pigment is added to the aqueous emulsion, coagulation of the aqueous emulsion is likely to occur. In this case, even when a coating formation promotor or an inorganic pigment can be mixed with the aqueous emulsion without suffering from the occurrence of coagulation, a coating obtained from the emulsion has poor gloss. Further, a large amount of stabilizing agent must be used and, therefore, the coating obtained from the emulsion has poor water resistance.

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[0004] As mentioned above, the conventional aqueous acrylate polymer emulsions have problems such that these emulsions have poor water resistance or poor weatherability, and coatings obtained from such emulsions having a pigment incorporated therein are unsatisfactory with respect to luster even just after the coating operation. Further, when the coating is exposed to outdoor conditions, especially ultraviolet light, for a prolonged period of time, the luster of the coating is drastically deteriorated. Further, there has recently been an increasing demand in the art for further improvement of various properties of aqueous acrylate polymer emulsions.

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SUMMARY OF THE INVENTION

[0005] In these situations, the present inventors have made extensive and intensive studies with a view toward solving the above-mentioned problems accompanying the conventional aqueous acrylate polymer emulsions. As a result, it has unexpectedly been found that an aqueous, silicone-modified acrylate polymer emulsion as mentioned below is capable of providing a coating which not only has excellent water resistance, but also can retain luster for a prolonged period of time. The above-mentioned aqueous, silicone-modified acrylate polymer emulsion consists in an acrylate polymer emulsion produced by subjecting a monomer system (A) to emulsion polymerization in an aqueous medium in the presence of an emulsifier (B), wherein said acrylate polymer emulsion is silicone-modified using a

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silicone structure-containing modifier (C) during or after said emulsion polymerization;

wherein said monomer system (A) comprises an acrylate monomer selected from the group consisting of an acrylic ester, a methacrylic ester and a mixture thereof, said acrylate monomer containing 5 % by weight or more, based on the weight of said monomer system (A), of a C₅-C₁₂ cycloalkyl ester of acrylic acid, a C₅-C₁₂ cycloalkyl ester of methacrylic acid, or a mixture thereof;

wherein said emulsifier (B) is selected from the group consisting of a sulfonic acid group-containing ethylenically unsaturated monomer, a sulfonate group-containing ethylenically unsaturated monomer, and a mixture thereof; and

wherein said silicone structure-containing modifier (C) comprises at least one silicone structure-containing silane (I) represented by the formula:



wherein R¹ represents a hydrogen atom, a C₁-C₁₆ aliphatic hydrocarbon group, a C₅-C₁₀ aryl group, a C₅-C₆ cycloalkyl group, a vinyl group, an acrylic C₁-C₁₀ alkyl group or a methacrylic C₁-C₁₀ alkyl group, and each R² independently represents a C₁-C₈ alkoxy group, an acetoxy group or a hydroxyl group and at least one member selected from the group consisting of a cyclic silane and a silane (III) represented by the formula:



wherein each R³ independently represents a hydrogen atom, a C₁-C₁₆ aliphatic hydrocarbon group, a C₅-C₁₀ aryl group, a C₅-C₆ cycloalkyl group, a vinyl group, an acrylic C₁-C₁₀ alkyl group or a methacrylic C₁-C₁₀ alkyl group, and each R⁴ independently represents a C₁-C₈ alkoxy group, an acetoxy group or a hydroxyl group; and wherein the molar ratio of said silane (I) to said at least one member selected from the group consisting of a cyclic silane and a silane (III) is at least 10/100.

[0006] Accordingly, it is an object of the present invention to provide a novel aqueous, silicone-modified acrylate polymer emulsion which is capable of providing a coating having excellent water repellency, water resistance, weatherability, dispersion characteristics of pigment, gloss retentivity, stain resistance and adhesion properties.

[0007] The foregoing and other objects, features and advantages will be apparent to those skilled in the art from the following detailed description and claims.

DETAILED DESCRIPTION OF THE INVENTION

[0008] According to the present invention, there is provided an aqueous, silicone-modified acrylate polymer emulsion as defined in claim 1.

[0009] In the aqueous, silicone-modified acrylate polymer emulsion of the present invention, it is preferred that the monomer system (A) and the emulsifier (B) be, respectively, used in an amount of from 80 to 99.95 % by weight, more preferably 90 to 99.9 % by weight, and in an amount of from 20 to 0.05 % by weight, more preferably from 10 to 0.1 % by weight, based on the total weight of the monomer system (A) and the emulsifier (B), and that the silicone structure-containing modifier (C) be used in an amount which satisfies the following relationships:

$$\frac{1}{2} \leq \frac{(A) + (B)}{(C)} \leq \frac{99}{1}$$

wherein (A), (B) and (C), respectively, represent amounts of the monomer system (A), the emulsifier (B) and the modifier (C) in terms of weight percentages based on the total weight of materials (A), (B) and (C).

[0010] Further, in the aqueous, silicone-modified acrylate polymer emulsion of the present invention, the ratio of the total weight of the monomer system (A), the emulsifier (B) and the modifier (C) to the weight of the aqueous medium is preferably 75/25 or less, more preferably from 30/70 to 70/30.

[0011] In the present invention, the monomer system (A) comprises an acrylate monomer selected from the group consisting of an acrylic ester, a methacrylic ester and a mixture thereof.

[0012] In the present invention, the monomer system (A) may further comprise a comonomer copolymerizable with the acrylate monomer, and which comonomer is at least one member selected from the group consisting of an acrylamide monomer, a methacrylamide monomer, a vinyl monomer and a carboxylic acid group-containing ethylenically unsaturated monomer. In the monomer system (A), it is preferred that the acrylate monomer and the comonomer be,

respectively, present in an amount of from 90 % to less than 100 % by weight and in an amount of from 10 % by weight or less, based on the total weight of the acrylate monomer and the comonomer.

[0013] Examples of (meth)acrylic esters which can be used in the present invention as the acrylate monomer of the monomer system (A) include a C₁-C₁₈ alkyl ester of (meth)acrylic acid, a C₁-C₁₈ hydroxyalkyl ester of (meth)acrylic acid, a (poly)oxyethylene mono(meth)acrylate having 1 to 100 ethylene oxide groups, a (poly)oxypropylene mono(meth)acrylate having 1 to 100 propylene oxide groups and a (poly)oxyethylene di(meth)acrylate having 1 to 100 ethylene oxide groups.

[0014] Specific examples of C₁-C₁₈ alkyl esters of (meth)acrylic acid include methyl (meth)acrylate, ethyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, 2-ethylhexyl (meth)acrylate and dodecyl (meth)acrylate. Specific examples of C₁-C₁₈ hydroxyalkyl esters of (meth)acrylic acid include 2-hydroxyethyl (meth)acrylate and 2-hydroxypropyl (meth)acrylate. Specific examples of (poly)oxyethylene mono(meth)acrylates include ethylene glycol (meth)acrylate, ethylene glycol methoxy(meth)acrylate, diethylene glycol (meth)acrylate, diethylene glycol methoxy(meth)acrylate, tetraethylene glycol (meth)acrylate and tetraethylene glycol methoxy(meth)acrylate. Specific examples of (poly)oxypropylene mono(meth)acrylates include propylene glycol (meth)acrylate, propylene glycol methoxy(meth)acrylate, dipropylene glycol (meth)acrylate, dipropylene glycol methoxy(meth)acrylate, tetrapropylene glycol (meth)acrylate and tetrapropylene glycol methoxy(meth)acrylate. Specific examples of (poly)oxyethylene di(meth)acrylates include ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate and tetraethylene glycol di(meth)acrylate. Specific examples of (meth)acrylic esters other than mentioned above include glycidyl (meth)acrylate and trimethylolpropane tri(meth)acrylate.

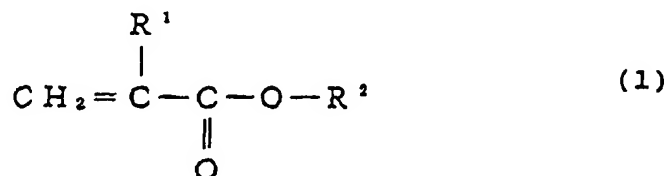
[0015] In the aqueous, silicone-modified acrylate polymer emulsion of the present invention, it is more preferred that the comonomer as an optional component of the monomer system (A) be a carboxylic acid group-containing ethylenically unsaturated monomer. Further, it is especially preferred that the carboxylic acid group-containing ethylenically unsaturated monomer be at least one member selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid and a half ester thereof, fumaric acid and a half ester thereof, and maleic acid and a half ester thereof. These carboxylic acid group-containing ethylenically unsaturated monomers are preferred because these monomers also function as a catalyst which facilitates the hydrolyzation reaction and condensation reaction of hydrolyzable silanes.

[0016] As mentioned above, in the present invention, as examples of comonomers which are copolymerizable with the acrylate monomer, in addition to the above-mentioned carboxylic acid group-containing ethylenically unsaturated monomers, there can be mentioned an acrylamide monomer, a methacrylamide monomer, a vinyl monomer and the like. Specific examples of acrylamide monomers and methacrylamide monomers include (meth)acrylamide, diacetone (meth)acrylamide, N-methylol (meth)acrylamide and N-butoxymethyl (meth)acrylamide. Specific examples of vinyl monomers include vinyl acetate, vinyl propionate, vinyl ester of versatic acid (manufactured sold by Shell Chemical Co., U.S.A. under the trade name of Veo Va), vinyl pyrrolidone, methyl vinyl ketone and a vinyl cyanide, such as acrylonitrile and methacrylonitrile.

[0017] Examples of comonomers other than mentioned above, which can be used in the present invention, include aromatic monomers, such as vinyl toluene, styrene and α -methylstyrene; halogenated vinyls, such as vinyl chloride and vinylidene chloride; butadiene; and ethylene.

[0018] In the present invention, the acrylate monomer of the monomer system (A) contains 5% or more, based on the weight of the monomer system (A), of a C₅-C₁₂ cycloalkyl ester of acrylic acid, a C₅-C₁₂ cycloalkyl ester of methacrylic acid or a mixture thereof, in which the cycloalkyl moiety of the cycloalkyl ester is unsubstituted or substituted with a C₁-C₆ alkyl group, a hydroxyl group or an epoxy group. In the present invention, when the monomer system (A) contains 5 % or more, based on the weight of the monomer system (A), of a C₅-C₁₂ cycloalkyl ester of acrylic acid, a C₅-C₁₂ cycloalkyl ester of methacrylic acid or a mixture thereof, the aqueous, silicone-modified acrylate polymer emulsion of the present invention can form a coating which is excellent especially with respect to weatherability.

[0019] Examples of the above-mentioned C₅-C₁₂ cycloalkyl esters of acrylic acid or methacrylic acid include compounds represented by formula (1):



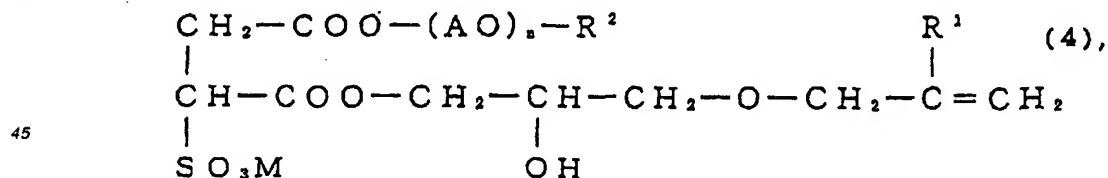
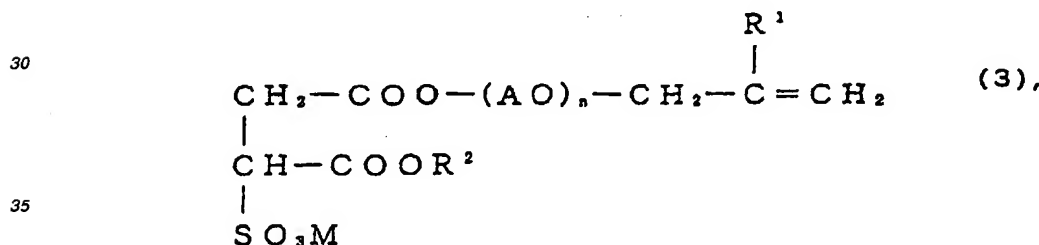
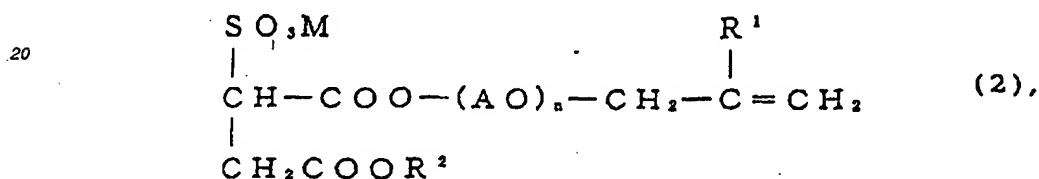
wherein R¹ represents a hydrogen atom or a methyl group; and R² represents a cyclopentyl group, a cyclohexyl

group or a cyclododecyl group, which is unsubstituted or substituted with a C₁-C₆ alkyl group, a hydroxyl group or an epoxy group.

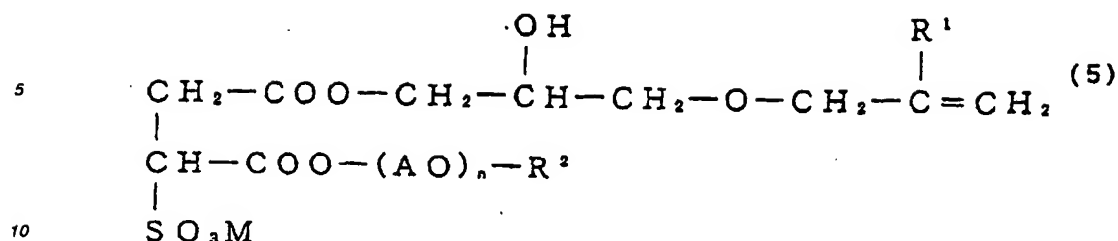
Specific examples of compounds represented by formula (1) above include cyclohexyl (meth)acrylate, 2-hydroxycyclohexyl (meth)acrylate, methylcyclohexyl (meth)acrylate and 2,3-epoxycyclohexane (meth)acrylate.

5 [0020] In the present invention, it is preferred that the sulfonic acid group- or sulfonate group-containing ethylenically unsaturated monomer of the emulsifier (B) be selected from radically polymerizable double bond-containing compounds having a sulfonic acid group, or an ammonium or an alkali metal salt thereof (i.e., ammonium sulfonate group or alkali metal sulfonate group). Among these compounds, more preferred are radically polymerizable double bond-containing compounds having a substituent selected from the group consisting of a C₁-C₂₀ alkyl group, a C₂-C₄ alkyl ether group, a poly-C₂-C₄ alkyl ether group, a C₆ or C₁₀ aryl group, and a succinic acid group, each of which is substituted with a sulfonic acid group which is in the form of an ammonium, a sodium or a potassium salt thereof, or vinyl sulfonate compounds having a vinyl group bonded to a sulfonic acid group which is in the form of an ammonium, a sodium or a potassium salt thereof.

10 [0021] Specific examples of compounds having a succinic acid group which is substituted with a sulfonic acid group which is in the form of an ammonium, a sodium or a potassium salt thereof include allylsulfosuccinates which, for example, can be represented by a formula selected from the following formulae (2), (3), (4) and (5):



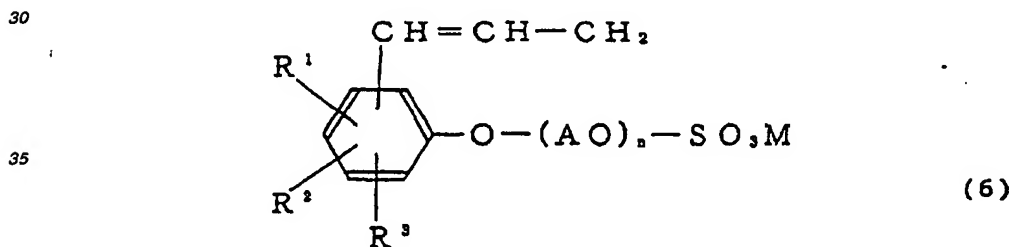
and



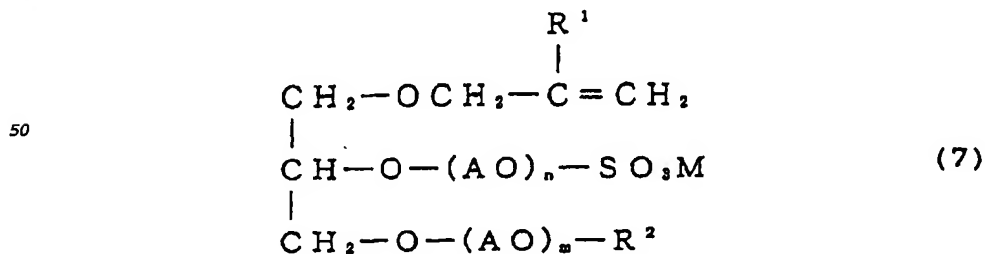
wherein R¹ represents a hydrogen atom or a methyl group; R² represents a hydrocarbon group, such as a C₁-C₂₀ alkyl group, a C₁-C₂₀ alkenyl group, a C₅-C₁₂ cycloalkyl group, a C₅-C₁₀ aryl group or a C₆-C₁₉ aralkyl group, each of which is unsubstituted or partially substituted with a hydroxyl group, a carboxyl group or the like, or an organic group containing an alkylene oxide, such as a polyoxyalkylene alkyl ether group (in which the alkylene moiety has 2 to 4 carbon atoms and the alkyl moiety has 0 to 20 carbon atoms) or a polyoxyalkylene alkylphenyl ether group (in which the alkylene moiety has 2 to 4 carbon atoms and an alkyl moiety has 0 to 20 carbon atoms); A represents the unsubstituted or substituted C₂-C₄ alkylene group; n represents an integer of from 0 to 200; and M represents an ammonium group, a sodium atom or a potassium atom.

[0022] Specific examples of commercially available products which comprise compounds represented by formulae (2) and (3) above include Eleminol® JS-2 (manufactured and sold by SANYO CHEMICAL INDUSTRIES, LTD., Japan). Specific examples of commercially available products which comprise compounds represented by formulae (4) and (5) above include Latemul® S-120, S-180A and S-180 (manufactured and sold by Kao Corp., Japan).

[0023] Specific examples of compounds having a C₂-C₄ alkyl ether group or a poly-C₂-C₄ alkyl ether group, each of which is substituted with a sulfonic acid group which is in the form of an ammonium, a sodium or a potassium salt thereof, include compounds represented by a formula selected from the following formulae (6) and (7):



wherein R¹ represents a C₆-C₁₈ alkyl, alkenyl or aralkyl group; R² represents a C₆-C₁₈ alkyl, alkenyl or aralkyl group; R³ represents a hydrogen atom or a propenyl group; A represents C₂-C₄ alkylene group; n represents an integer of from 1 to 200; and M represents an ammonium group, a sodium atom or a potassium atom, and



wherein R¹ represents a hydrogen atom or a methyl group; R² represents a C₈-C₂₄ alkyl or acyl group; A represents C₂-C₄ alkylene group; n represents an integer of from 0 to 20; m represents an integer of from 0 to 50; and M

represents an ammonium group, a sodium atom or a potassium atom.

[0024] Specific examples of alkylphenol ether compounds represented by formula (6) above include Aquaron® HS-10 (manufactured and sold by Dai-ichi Kogyo Seiyaku Co., Ltd., Japan). Specific examples of compounds represented by formula (7) above include Adeka Rea soap® SE-1025N (manufactured and sold by ASAHI DENKA KOGYO K.K., Japan).

[0025] Specific examples of compounds having a C₆ or C₁₀ aryl group which is substituted with a sulfonate group include a p-styrenesulfonic acid which is in the form of an ammonium, a sodium or a potassium salt thereof. Specific examples of compounds having a C₁-C₂₀ alkyl group which is substituted with a sulfonate group include methylpropanesulfonacrylamide which is in the form of an ammonium, a sodium or a potassium salt thereof, a sulfoalkyl acrylate which is in the form of an ammonium, a sodium or a potassium salt thereof, and sulfoalkyl methacrylate which is in the form of an ammonium, a sodium or potassium salt thereof. Specific examples of sulfonate group-containing compounds other than mentioned above include a vinyl sulfonate compound having a vinyl group bonded to a sulfonic acid group which is in the form of an ammonium, a sodium or a potassium salt thereof.

[0026] The ethylenically unsaturated monomer used as emulsifier (B) can be present in the emulsion in any of the following states:

(i) the ethylenically unsaturated monomer is present in the emulsion as a copolymer thereof with the emulsified particles of the acrylate polymer emulsion, which copolymer is formed by radical polymerization;

(ii) the ethylenically unsaturated monomer is adsorbed on the emulsified particles of the acrylate polymer emulsion or present in the aqueous phase of the acrylate polymer emulsion, in the form of an unreacted monomer; and

(iii) the ethylenically unsaturated monomer is adsorbed on the emulsified particles of the acrylate polymer emulsion or present in the aqueous phase of the acrylate polymer emulsion, in the form of a copolymer thereof with a water-soluble monomer or a polymer of the ethylenically unsaturated monomers.

In this connection, it is noted that the higher the ratio of the ethylenically unsaturated monomers which are present in state (i) above, the higher the water resistance of the coating formed from the final emulsion.

[0027] The ethylenically unsaturated monomer used as emulsifier (B) can be identified by subjecting a coating obtained from the emulsion to a pyrolysis gas chromatography/mass spectrometry (Py-GC-MS) or a pyrolysis mass spectrometry (Py-MS). Alternatively, the ethylenically unsaturated monomers can be identified by a method in which the aqueous phase is separated from the emulsion and the residue is subjected to fast atom bombardment mass spectrometry (FAB mass spectrometry).

[0028] In the present invention, the silicone structure-containing modifier (C) comprises at least one silicone structure-containing silane (I) represented by the formula:



wherein R¹ represents a hydrogen atom, a C₁-C₁₆ aliphatic hydrocarbon group, a C₅-C₁₀ aryl group, a C₅-C₆ cycloalkyl group, a vinyl group, an acrylic C₁-C₁₀ alkyl group or a methacrylic C₁-C₁₀ alkyl group, and each R² independently represents a C₁-C₈ alkoxy group, an acetoxy group or a hydroxyl group.

and at least one member selected from the group consisting of a cyclic silane and a silane (III) (as defined of below). [0029] The term "(meth)acrylic alkyl group" used herein means a group derived from an alkyl (meth)acrylate, in which group the alkyl moiety has a free valence.

[0030] In formula (I) above, it is preferred that R¹ represent a methyl group, a phenyl group, a vinyl group or a γ-(meth)acryloxypropyl group and each R² independently represent a methoxyl group, an ethoxyl group a propoxyl group, a methoxyethoxyl group or a hydroxyl group. Preferred specific examples of silanes (I) represented by formula (I) above include methyltrimethoxysilane, phenyltrimethoxysilane, methyltriethoxysilane, phenyltriethoxysilane, isobutyltrimethoxysilane, vinyltriethoxysilane, γ-acryloxypropyltrimethoxysilane, γ-acryloxypropyltriethoxysilane, γ-methacryloxypropyltrimethoxysilane and γ-methacryloxypropyltriethoxysilane. These silanes may be contained in modifier (C) individually or in combination.

[0031] In the present invention, the silicone structure-containing modifier (C) may further comprise at least one member selected from the group consisting of a hydrolyzable group-containing linear siloxane and a silane (II) represented by the formula:



wherein each R^3 independently represents a hydrogen atom, a C_1 - C_{16} aliphatic hydrocarbon group, a C_5 - C_{10} aryl group, a C_5 - C_6 cycloalkyl group, a vinyl group, an acrylic C_1 - C_{10} alkyl group or a methacrylic C_1 - C_{10} alkyl group, each R^4 independently represents a C_1 - C_8 alkoxy group, an acetoxy group or a hydroxyl group, and n is 0 or 3.

[0032] The molar ratio of the silane (I) to the total of said at least one member selected from the group consisting of the cyclic silane and the silane (III), and said at least one member selected from the group consisting of the hydrolyzable group-containing linear siloxane and the silane (II) is at least 10/100, preferably 35/100 or more.

[0033] As mentioned above, the silicone structure-containing modifier (C) comprises at least one member selected from the group consisting of a cyclic silane and a silane (III) represented by the formula:



wherein each R^3 independently represents a hydrogen atom, a C_1 - C_{16} aliphatic hydrocarbon group, a C_5 - C_{10} aryl group, a C_5 - C_6 cycloalkyl group, a vinyl group, an acrylic C_1 - C_{10} alkyl group or a methacrylic C_1 - C_{10} alkyl group, and each R^4 independently represents a C_1 - C_8 alkoxy group, an acetoxy group or a hydroxyl group.

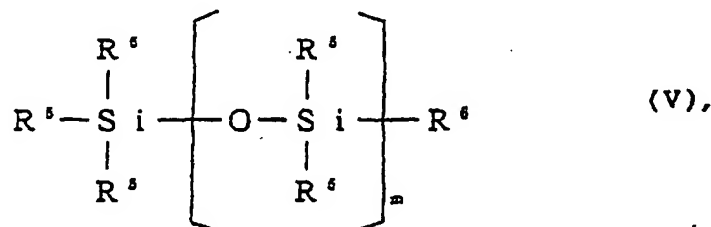
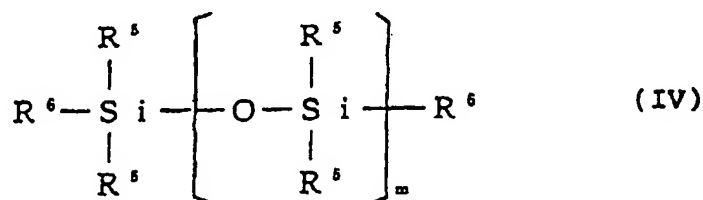
[0034] The molar ratio of the silane (I) to at least one member selected from the group consisting of a cyclic silane and a silane (III) is at least 10/100, preferably 35/100 or more.

[0035] In formulae (II) and (III) above, it is especially preferred that each R^3 independently represent a methyl group or a phenyl group, and each R^4 independently represent a methoxy group, an ethoxy group, a propoxy group, a butoxy group, a methoxyethoxy group or a hydroxyl group.

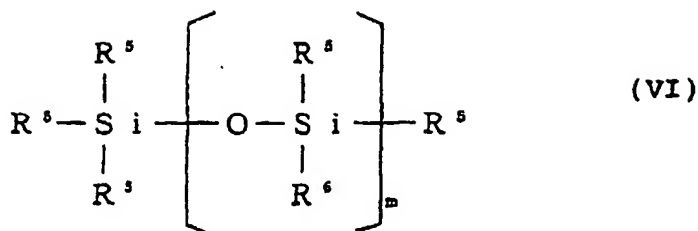
[0036] By the use of silane (III) or a cyclic silane in combination with silane (I), it becomes possible to lower the cross-linking density of a silicone polymer formed from modifier (C), thereby preventing the silicone polymer from having a complicated structure, so that a coating obtained from the emulsion can be imparted with a softness.

[0037] Specific examples of silanes of formula (II), exclusive of those which are represented by formula (III), include phenyltrimethoxysilane, trimethylmethoxysilane and tetraethoxysilane.

[0038] Examples of hydrolyzable group-containing linear siloxanes include compounds represented by a formula selected from the following formulae (IV), (V) and (VI):



and



wherein each R^5 independently represents a hydrogen atom, a C_1 - C_{16} aliphatic hydrocarbon group, a C_5 - C_{10} aryl group, a C_5 or C_6 cycloalkyl group, a vinyl group, an acrylic C_1 - C_{10} alkyl group or a methacrylic C_1 - C_{10} alkyl group; each R^6 independently represents a C_1 - C_8 alkoxy group, an acetoxy group, a hydroxyl group, an epoxy group or an ethylene oxide group; and m represents an integer of from 1 to 999.

[0039] Specific examples of silane (III) include dimethyldimethoxysilane, diphenyldimethoxysilane, dimethyldiethoxysilane, diphenyldiethoxysilane, methylphenyldimethoxysilane and γ -methacryoxypropylmethyldimethoxysilane.

[0040] Examples of cyclic silanes which can be used in the present invention include octamethylcyclotetrasiloxane, octaphenylcyclotetrasiloxane, hexamethylcyclotrisiloxane, decamethylcyclopentasiloxane and tetramethyltetravinylcyclotetrasiloxane. With respect to these cyclic silanes, reference can be made to Canadian Patent No. 842947.

[0041] In addition to at least one compound selected from the group consisting of the above-mentioned silane (II), silane (III), cyclic silane and linear siloxane, the modifier (C) can further comprise a chlorosilane, such as methylchlorosilane, methyldichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, phenyltrichlorosilane, diphenylchlorosilane, vinylchlorosilane, γ -(meth)acryloxypropyltrichlorosilane and γ -(meth)acryloxypropyldichloromethylsilane.

[0042] In the present invention, when the above-mentioned modifier (C) is introduced into an emulsion polymerization system comprising the monomer system (A) and the specific emulsifier (B), the silane undergoes hydrolysis and condensation, so that a silicone is formed in the emulsified particles of the acrylate polymer emulsion obtained. Accordingly, due to the silicone formed in the emulsified particles of the acrylate polymer emulsion, a coating formed from the emulsion has an extremely excellent weatherability and gloss retentivity. For example, when a coating formed from a paint comprising a conventional acrylic emulsion having a titanium dioxide or the like incorporated therein is exposed to outdoor conditions for a prolonged period of time, the coating rapidly loses luster, and also exhibits a low gloss retentivity, whereas, even when a coating obtained from a paint comprising the aqueous, silicone-modified acrylate polymer emulsion of the present invention having a titanium dioxide or the like incorporated therein is exposed to outdoor conditions, the coating is unlikely to lose luster, and exhibits excellent gloss retentivity.

[0043] The presence of the above-mentioned condensation product of silane can be identified by means of ^{29}Si -NMR (^{29}Si nuclear magnetic resonance) or ^1H -NMR (proton nuclear magnetic resonance). For example, the presence of the condensation product of silane (I) can be identified by the presence of a peak at -40 to -80 ppm in terms of the chemical shift of ^{29}Si -NMR. The presence of the condensation product of silane (III) or a cyclic silane is identified by the presence of a peak at -16 to -26 ppm in terms of the chemical shift of ^{29}Si -NMR.

[0044] In the present invention, it is preferred that the modifier (C) be added to the emulsion polymerization system, so that the silicone-modification of the emulsion is performed during the emulsion polymerization.

[0045] According to a preferred embodiment of the present invention, there is provided an aqueous, silicone-modified acrylate emulsion, wherein the monomer system (A) is comprised of monomer systems (A^1) and (A^2), each comprising the acrylate monomer, and the emulsifier (B) is comprised of emulsifiers (B^1) and (B^2), each selected from the group consisting of the sulfonic acid group-containing ethylenically unsaturated monomer, the sulfonate group-containing ethylenically unsaturated monomer, and a mixture thereof with the proviso that monomer systems (A^1) and (A^2) are the same or different, and emulsifiers (B^1) and (B^2) are the same or different, and wherein the emulsion polymerization is conducted in a sequence of step (1) and step (2), wherein in step (1), the monomer system (A^1) is subjected to emulsion polymerization in an aqueous medium in the presence of the emulsifier (B^1) to thereby obtain a preliminary aqueous acrylate polymer emulsion having a seed latex dispersed therein, and in step (2), the monomer system (A^2) and the emulsifier (B^2), optionally with an aqueous medium, are added to the preliminary aqueous acrylate polymer emulsion to effect emulsion polymerization thereof, thereby producing a final aqueous acrylate polymer emulsion, wherein the silicone-modification is performed using the silicone structure-containing modifier (C) during or after the emulsion polymerization.

[0046] In step (2) above, the modifier (C) can be added to the emulsion polymerization system to thereby perform the silicone-modification during the emulsion polymerization. Alternatively, the final aqueous acrylate emulsion can be treated with the modifier (C) to thereby perform the silicone-modification after the emulsion polymerization.

[0047] In step (1) above, the monomer system (A^1) and the emulsifier (B^1) can be, respectively, used in an amount

of from 80 to 99.95 % by weight, preferably from 90 to 99.9 % by weight, and in an amount of from 0.05 to 20 % by weight, preferably from 0.1 to 10 % by weight, based on the total weight of the monomer system (A¹) and the emulsifier (B¹). In step (2) above, the monomer system (A²) and the emulsifier (B²) can be, respectively, used in an amount of from 80 to 99.95 % by weight, preferably from 90 to 99.9 % by weight, and in an amount of from 0.05 to 20 % by weight, preferably from 0.1 to 10 % by weight, based on the total weight of the monomer system (A²) and the emulsifier (B²). The silicone structure-containing-modifier (C) can be used in an amount which satisfies the following relationships:

$$\frac{1}{2} \leq \frac{(A^1) + (A^2) + (B^1) + (B^2)}{(C)} \leq \frac{99}{1}$$

wherein (A¹), (A²), (B¹), (B²) and (C), respectively, represent amounts of monomer system (A¹), monomer system (A²), emulsifier (B¹), emulsifier (B²) and modifier (C) in terms of weight percentages, based on the total weight of materials (A¹), (A²), (B¹), (B²) and (C).

[0048] The ratio of the total weight of the monomer system (A¹) and the emulsifier (B¹) to the total weight of the monomer system (A²) and the emulsifier (B²) is from 1/99 to 99/1, preferably from 5/95 to 95/5.

[0049] When (A¹), (A²), (B¹), (B²) and (C) are used in the amount relationships as defined above, the emulsion can be very stably obtained and the obtained emulsion is capable of forming a coating which has especially excellent water resistance and weatherability.

[0050] In step (1) above, it is preferred that the monomer system (A¹) contain 0.5 to 30 % by weight, more preferably 1 to 20 % by weight, of a carboxylic acid group-containing ethylenically unsaturated monomer, based on the weight of the monomer system (A¹). In step (2) above, the monomer system (A²) may or may not contain 1 to 2 % by weight of a carboxylic acid group-containing ethylenically unsaturated monomer, based on the weight of the monomer system (A²). The above-mentioned carboxylic acid group-containing ethylenically unsaturated monomer can be preferably employed, since it functions also as a catalyst to facilitate the hydrolyzation reaction and condensation reaction of the above-mentioned hydrolyzable group-containing silane.

[0051] In the present invention, it is preferred that the silicon content of a polymer comprising components (A), (B) and (C) be from 1 to 10 % by weight, based on the weight of the polymer. When the silicon content is within the range as mentioned above, the emulsion can be very stably obtained, and the obtained emulsion can form a coating which has especially excellent water resistance and weatherability.

[0052] For producing the aqueous, silicone-modified acrylate polymer emulsion of the present invention, a conventional emulsion polymerization method can be employed. However, in the case where, in accordance with the above-mentioned preferred embodiment, the emulsion polymerization is conducted in a sequence of two steps [step (1) and step (2)] [wherein a preliminary aqueous acrylate polymer emulsion having a seed latex dispersed therein is prepared in step (1), and the preliminary aqueous acrylate polymer emulsion obtained in step (1) is further subjected to emulsion polymerization in step (2)], the two-step emulsion polymerization can be practiced in either of the following two manners (i) and (ii):

(i) the modifier (C) is added to the preliminary aqueous acrylate polymer emulsion having a seed latex dispersed therein at the same temperature as used in the polymerization of the preliminary aqueous acrylate polymer emulsion, and subsequently, each of the monomer system (A²) and emulsifier (B²) is introduced to the reaction system at a time or in a stepwise manner during the course of polymerization of a silane of the modifier (C); and

(ii) each of the modifier (C), monomer system (A²) and emulsifier (B²) is simultaneously added at a time or in a stepwise manner to the preliminary aqueous acrylate emulsion having a seed latex dispersed therein at the same temperature as used in the polymerization of the preliminary aqueous acrylate polymer emulsion. These two manners can be employed individually or in combination. The manner of two-step emulsion polymerization is not limited to the above two manners.

[0053] Generally, the hydrogen ion concentration during the preparation of the preliminary aqueous acrylate polymer emulsion in step (1) and during the emulsion polymerization in step (2) is adjusted so as to give a pH value of 4.0 or less, preferably 3.0 or less.

[0054] In the present invention, the emulsion polymerization is conducted in an aqueous medium. As an aqueous medium, water is generally used. Alternatively, an aqueous solution of a water-soluble solvent, such as a lower alcohol having 1 to 3 carbon atoms or acetone, can be employed as an aqueous medium. In this case, the content of the solvent in the emulsion is preferably 20 % or less. With respect to the obtained final emulsion, it is preferred that weight ratio of dispersed phase (solids) to aqueous medium as a dispersion medium be 70/30 or less, more preferably from 30/70 to 65/35.

[0055] In practicing the emulsion polymerization, a compound, which is decomposable by heat or a reducing agent

to generate radicals and thereby initiate an addition polymerization reaction of the ethylenically unsaturated monomer, can be advantageously employed as a radical polymerization catalyst. Examples of such compounds include a water-soluble or oil-soluble persulfates, peroxides, and azobis compounds. Specific examples of such compounds include potassium persulfate, sodium persulfate, ammonium persulfate, hydrogen peroxide, t-butyl hydroperoxide, t-butyl peroxybenzoate, 2,2-azobisisobutyronitrile, 2,2-azobis(2-diaminopropane)hydrochloride and 2,2-azobis(2,4-dimethylvaleronitrile). Of these, especially preferred are potassium persulfate, sodium persulfate and ammonium persulfate, which are effective also as a catalyst to facilitate the hydrolysis reaction and condensation reaction of the hydrolyzable silane. The radical polymerization catalyst is generally used in an amount of from 0.1 to 1 % by weight, based on the weight of the ethylenically unsaturated monomer.

[0056] Generally, it is preferred that emulsion polymerization be conducted at a temperature of from 65 to 90 °C under atmospheric pressure. However, the emulsion polymerization can be conducted under high pressure, so as to, for example, prevent the monomers from being vaporized at the polymerization temperature. The polymerization time comprises an introduction time and a maturation (cooking) time. With respect to the introduction time, when each of the materials is introduced to a reaction system at a time, the introduction time is generally several minutes. When the raw materials are stepwise introduced to a reaction system, the introduction of the raw materials is conducted in a manner such that the heat generated in the polymerization reaction can be removed. Therefore, in this case, the introduction time may vary, depending on the desired content of the polymer in a final emulsion. However, the introduction time is generally 10 minutes or more. With respect to the maturation (cooking) time, it is preferred that the maturation time be 10 minutes or more. When the polymerization time is shorter than the period of time as mentioned above, there is a danger that not only do the raw materials remain unreacted, but also the hydrolyzable silanes are not condensed and remain as they are. When it is desired to increase the rate of polymerization or when it is desired to perform a polymerization reaction at a temperature as low as 70 °C or less, it is advantageous to use a reducing agent, such as sodium bisulfite, ferrous chloride, ascorbate and Rongalit, in combination with a radical polymerization catalyst. Further, if desired, in order to control the molecular weight of the polymer, a chain transfer agent, such as dodecylmercaptan, can be used.

[0057] In the present invention, in addition to the above-mentioned emulsifier (B) which is selected from the group consisting of a sulfonic acid group-containing ethylenically unsaturated monomer, the sulfonate group-containing ethylenically unsaturated monomer, and a mixture thereof, a conventional surfactant can be used in combination with the emulsifier (B). Examples of conventional surfactants which can be used in combination with the emulsifier (B) include anionic surfactants, such as a fatty acid soap, an alkyl sulfonate, an alkyl sulfosuccinate, a polyoxyethylene alkyl sulfate, a polyoxyethylene alkylaryl sulfate; non-reactive nonionic surfactants, such as a polyoxyethylene alkylaryl ether, a sorbitan fatty acid ester of polyoxyethylene and an oxyethylene-oxypropylene block copolymer; and reactive nonionic surfactants, such as α -{1-[(allyloxy)methyl]-2-(nonylphenoxy)ethyl}- ω -hydroxypolyoxyethylene [e.g., Adeka Rea soap NE-20, NE-30 and NE-40 (manufactured and sold by ASAHI DENKA KOGYO K.K., Japan)], a polyoxyethylene alkylpropenylphenylether [e.g., Aquaron RN-10, RN-20, RN-30 and RN-50 (manufactured and sold by Dai-ichi Kogyo Seiyaku Co., Ltd., Japan)].

[0058] With respect to the amount of the conventional surfactant in terms of % by weight, based on the weight of the emulsion: an anionic surfactant can be used in an amount of 0.5 % by weight or less, preferably 0.25 % by weight or less, more preferably 0.1 % by weight or less; and a non-reactive nonionic surfactant or a reactive nonionic surfactant can be used in an amount of 2.0 % by weight or less, preferably 1.0 % by weight or less, more preferably 0.5 % by weight or less. When the conventional surfactants are used in amounts which exceed the above ranges, a coating formed from the obtained aqueous, silicone-modified acrylate polymer emulsion has disadvantageously low water resistance.

[0059] In the present invention, after the termination of emulsion polymerization, a curing catalyst can be added to the aqueous, silicone-modified acrylate polymer emulsion to facilitate the formation of a coating. Examples of curing catalysts usable in the present invention include metal salts, such as dibutyltin dilaurate, dioctyltin dilaurate, dibutyltin diacetate, tin octylate, tin laurate, iron octylate, lead octylate and tetrabutyl titanate; and amine compounds, such as n-hexylamine and 1,8-diazabicyclo[5,4,0]-7-undecene.

[0060] When a water-insoluble curing catalyst is used, it is desirable that such a catalyst be emulsified using a surfactant and water prior to use.

[0061] In the present invention, from the viewpoint of maintaining the dispersion stability of the aqueous, silicone-modified acrylate polymer emulsion for a prolonged period of time, it is preferred that the pH value of the emulsion be adjusted to 5 to 10, using ammonia, sodium hydroxide, potassium hydroxide, and amines, such as dimethylaminoethanol.

[0062] In the aqueous, silicone-modified acrylate polymer emulsion of the present invention, it is preferred that the average particle diameter of the dispersed phase be from 10 to 1000 nm.

[0063] The aqueous, silicone-modified acrylate emulsion of the present invention can be advantageously used as a paint, an undercoating or finish coating material for building materials, an adhesive, a pressure-sensitive adhesive, a

processing agent for papers, or a finish coating material for textile fabrics. Especially, the aqueous, silicone-modified acrylate emulsion of the present invention can be advantageously used as a paint, or a finish coating material for building materials.

[0064] If desired, other components, which are conventionally used in aqueous paints, e.g., a coating formation promoter, a thickening agent, an anti-foaming agent, a pigment, a dispersant, a dye and an antiseptic agent, can be added to the aqueous, silicone-modified acrylate polymer emulsion of the present invention.

Best Mode for Carrying Out the Invention

[0065] Hereinbelow, the present invention will be described in more detail with reference to the following Examples and Comparative Examples, but they should not be construed as limiting the scope of the present invention.

[0066] In Examples and Comparative Examples, the "part(s)" and "%" are given by weight unless otherwise specified. Further, with respect to the properties of the aqueous, silicone-modified acrylate polymer emulsions obtained in Examples and Comparative Examples, sample paints having the following composition were prepared using respective emulsions, and examination was made in accordance with the methods described below.

Composition for paint	
Pigment dispersion	
Water	82.5 parts
Poiz 530 (dispersant: manufactured and sold by Kao Corp., Japan)	7.5 parts
5 % aqueous solution of sodium tripolyphosphate	7.5 parts
3 % aqueous solution of Daicel HEC SP-600 (thickening agent: manufactured and sold by Daicel Chemical Industries, Ltd., Japan)	25.0 parts
Nopco 1497VD (anti-foaming agent: manufactured and sold by San Nopco K.K., Japan)	2.5 parts
TiPaque R-930 (rutile titanium oxide: manufactured and sold by ISHIHARA SANGYO KAISHA, LTD., Japan)	375.0 parts
Let-down components	
Emulsion (solids component)	460.0 parts
Ethylene glycol monobutyl ether	60.0 parts
Ethylene glycol mono(2-ethylhexyl) ether	10.0 parts
Water	30.0 parts
Nopco 1497VD	1.0 parts

Examination Method

(i) Initial gloss value and gloss retentivity

[0067] The above-mentioned pigment dispersion and let-down components are mixed, thereby preparing a paint. The obtained paint was coated on an anodized aluminium plate (anodized by sulfuric acid) by means of wire coater No. 50, and dried at room temperature for 30 days. The initial gloss value of the coated paint (coating) was measured in terms of the 60° - 60° mirror reflectance (%) (each of angle of incidence and angle of reflection: 60°) (the time when the measurement was conducted is defined as the initiation time of examination, i.e., 0 hour after the initiation of the examination). Subsequently, the coating was subjected to an exposure test (rainfall cycle: 12 min/hr; temperature of black panel: 60 - 66 °C) by means of a sunshine-type weatherometer (WEL-SUN-DC: manufactured and sold by Suga Shiken-ki K.K., Japan). The final gloss value of the coating was measured in terms of the 60° - 60° mirror reflectance (%) after 3000 hours of exposure. The percentage of the final gloss value based on the initial gloss value is defined as the gloss retentivity.

(ii) Water resistance

[0068] A paint prepared in substantially the same manner as in (i) above was coated on an anodized aluminium plate (anodized by sulfuric acid) by means of wire coater No. 50 and dried at room temperature for 2 hours. The coated paint was further dried at 50 °C for 2 days and, then, immersed in water having a temperature of 40 °C for 30 days. The condition of the coated paint (coating) was evaluated by visual observation in terms of the following 4 criteria.

Criteria

[0069]

- 5 ⊙ : No blistering or lowering of luster is observed.
 ○ : Slight blistering is observed, but no lowering of luster is observed.
 Δ : Blistering and lowering of luster are observed.
 × : Blistering is observed on overall surface of the coating, and luster is markedly lowered.

10 Comparative Example 1

[0070] 300 Parts of water, 52 parts of methyl methacrylate, 40 parts of butyl acrylate, 8 parts of methacrylic acid and 20 parts of a 20 % aqueous solution of Latemul S-180A (ammonium salt of diester of sulfosuccinic acid, which has a double bond and is copolymerizable with an ethylenically unsaturated monomer) (manufactured and sold by Kao Corp., Japan) were charged in a reactor having a stirrer, a reflux condenser, dropping tanks and a thermometer. After elevating the temperature in the reactor to 78 °C, 0.5 part of ammonium persulfate was added to the reactor, and the resultant mixture was allowed to stand for 1 hour, thereby obtaining a preliminary aqueous acrylate polymer emulsion having a seed latex dispersed therein. The hydrogen ion concentration of the obtained preliminary aqueous acrylate polymer emulsion was measured to give a pH value of 1.8. Then, 2 types of liquid mixtures, i.e., a liquid mixture of 330 parts of water, 207 parts of methyl methacrylate, 190 parts of butyl acrylate, 3 parts of methacrylic acid, 20 parts of a 20 % aqueous solution of Latemul S-180A and 1.0 part of ammonium persulfate, and a liquid mixture of 2.5 parts of γ-methacryloxypropyltrimethoxysilane, 25 parts of dimethyldimethoxysilane and 25 parts of methyltrimethoxysilane, were individually dropped into the reactor from separate dropping tanks over 3 hours. During the dropping of the above-mentioned liquid mixtures into the reactor, the temperature in the reactor was maintained at 80 °C. After completion of the dropping of the liquid mixtures into the reactor, the temperature in the reactor was elevated to 85 °C and the mixture was allowed to stand for 6 hours. After cooling the mixture in the reactor to room temperature, the hydrogen ion concentration thereof was measured to give a pH value of 2.1. A 25 % aqueous solution of ammonia was added to the mixture in the reactor to thereby adjust the pH value thereof to 8. Then, the resultant mixture was filtered by means of a 100-mesh metal wire net to thereby obtain a final aqueous, silicone-modified acrylate polymer emulsion. The amount of filtered-off aggregates was as small as 0.02 % by weight (on a dry basis), based on the total weight of the monomers. With respect to the obtained emulsion, the solids content of the emulsion was 44.0 %, and the average particle diameter of the dispersed phase of the emulsion was 1080 Å. Using this emulsion, a paint was prepared, and the paint thus prepared was examined with respect to the initial gloss value, gloss retentivity and water resistance. Results are shown in Table 1.

35 Example 1

[0071] 300 Parts of water, 37 parts of methyl methacrylate, 40 parts of butyl acrylate, 15 parts of cyclohexyl methacrylate, 8 parts of methacrylic acid and 20 parts of a 20 % aqueous solution of Latemul S-180A (ammonium salt of diester of sulfosuccinic acid, which has a double bond and is copolymerizable with an ethylenically unsaturated monomer) (manufactured and sold by Kao Corp., Japan) were charged in a reactor having a stirrer, a reflux condenser, dropping tanks and a thermometer. After elevating the temperature in the reactor to 78 °C, 0.5 part of ammonium persulfate was added to the reactor, and the resultant mixture was allowed to stand for 1 hour, thereby obtaining a preliminary aqueous acrylate polymer emulsion having a seed latex dispersed therein. The hydrogen ion concentration of the obtained preliminary aqueous acrylate polymer emulsion was measured to give a pH value of 1.8. Then, 2 types of liquid mixtures, i.e., a liquid mixture of 330 parts of water, 177 parts of methyl methacrylate, 160 parts of butyl acrylate, 60 parts of cyclohexyl methacrylate, 3 parts of methacrylic acid, 20 parts of a 20 % aqueous solution of Latemul S-180A and 1.0 part of ammonium persulfate, and a liquid mixture of 2.5 parts of γ-methacryloxypropyltrimethoxysilane, 25 parts of dimethyldimethoxysilane and 25 parts of methyltrimethoxysilane, were individually dropped into the reactor from separate dropping tanks over 3 hours. During the dropping of the above-mentioned liquid mixtures into the reactor, the temperature in the reactor was maintained at 80 °C. After completion of the dropping of the liquid mixtures into the reactor, the temperature in the reactor was elevated to 85 °C and the mixture was allowed to stand for 6 hours. After cooling the mixture in the reactor to room temperature, the hydrogen ion concentration thereof was measured to give a pH value of 2.1. A 25 % aqueous solution of ammonia was added to the mixture in the reactor to thereby adjust the pH value thereof to 8. Then, the resultant mixture was filtered by means of a 100-mesh metal wire net to thereby obtain a final aqueous, silicone-modified acrylate polymer emulsion. The amount of filtered-off aggregates was as small as 0.02 % by weight (on a dry basis), based on the total weight of the monomers. With respect to the obtained emulsion, the solids content of the emulsion was 44.0 %, and the average particle diameter of the dispersed phase of the emulsion

was 1080 Å. Using this emulsion, a paint was prepared, and the paint thus prepared was examined with respect to the initial gloss value, gloss retentivity and water resistance. Results are shown in Table 1.

Comparative Example 2

[0072] 300 Parts of water, 52 parts of methyl methacrylate, 40 parts of n-butyl acrylate, 8 parts of methacrylic acid, 4 parts of a 40 % aqueous solution of sodium dioctylsulfosuccinate (Pelex® OT-P: manufactured and sold by Kao Corp., Japan) and 1 part of a 25 % aqueous solution of polyoxyethylene nonylphenyl ether (Emulgen® 950: manufactured and sold by Kao Corp., Japan) were charged in a reactor having a stirrer, a reflux condenser, dropping tanks and a thermometer. After elevating the temperature in the reactor to 78 °C, 0.5 part of ammonium persulfate was added to the reactor, and the resultant mixture was allowed to stand for 1 hour, thereby obtaining a preliminary aqueous acrylate polymer emulsion having a seed latex dispersed therein. The hydrogen ion concentration of the obtained preliminary aqueous acrylate polymer emulsion was measured to give a pH value of 1.8. Then, 2 types of liquid mixtures, i.e., a liquid mixture of 330 parts of water, 207 parts of methyl methacrylate, 190 parts of n-butyl acrylate, 3 parts of methacrylic acid, 5 parts of a 25 % aqueous solution of polyoxyethylene nonylphenyl ether (Emulgen® 950: manufactured and sold by Kao Corp., Japan) and 1.0 part of ammonium persulfate, and a liquid mixture of 2.5 parts of γ -methacryloxypropyltrimethoxysilane, 25 parts of dimethyldimethoxysilane and 25 parts of methyltrimethoxysilane, were individually dropped into the reactor from separate dropping tanks over 3 hours. During the dropping of the above-mentioned liquid mixtures into the reactor, the temperature in the reactor was maintained at 80 °C. After completion of the dropping of the liquid mixtures into the reactor, the temperature in the reactor was elevated to 85 °C and the mixture was allowed to stand for 6 hours. After cooling the mixture in the reactor to room temperature, the hydrogen ion concentration thereof was measured to give a pH value of 2.2. A 25 % aqueous solution of ammonia was added to the mixture in the reactor to thereby adjust the pH value thereof to 8. Then, the resultant mixture was filtered by means of a 100-mesh metal wire net to thereby obtain a final emulsion. The amount of filtered-off aggregates was as small as 0.02 % by weight (on a dry basis), based on the total weight of the monomers. With respect to the obtained emulsion, the solids content of the emulsion was 44.1 %, and the average particle diameter of the dispersed phase of the emulsion was 1050 Å. Using this emulsion, a paint was prepared, and the paint thus prepared was examined with respect to the initial gloss value, gloss retentivity and water resistance. Results are shown in Table 1.

Comparative Example 3

[0073] 300 Parts of water, 52 parts of methyl methacrylate, 40 parts of butyl acrylate, 8 parts of methacrylic acid and 20 parts of a 20 % aqueous solution of Latemul S-180A (ammonium salt of diester of sulfosuccinic acid, which has a double bond and is copolymerizable with an ethylenically unsaturated monomer) (manufactured and sold by Kao Corp., Japan) were charged in a reactor having a stirrer, a reflux condenser, dropping tanks and a thermometer. After elevating the temperature in the reactor to 78 °C, 0.5 part of ammonium persulfate was added to the reactor, and the resultant mixture was allowed to stand for 1 hour, thereby obtaining a preliminary aqueous acrylate polymer emulsion having a seed latex dispersed therein. The hydrogen ion concentration of the obtained preliminary aqueous acrylate polymer emulsion was measured to give a pH value of 1.8. Then, a liquid mixture of 330 parts of water, 207 parts of methyl methacrylate, 190 parts of butyl acrylate, 3 parts of methacrylic acid, 20 parts of a 20 % aqueous solution of Latemul S-180A and 1.0 part of ammonium persulfate, and 50 parts of dimethyldimethoxysilane were individually dropped into the reactor from separate dropping tanks over 3 hours. During the dropping of the above-mentioned liquid mixture and dimethyldimethoxysilane into the reactor, the temperature in the reactor was maintained at 80 °C. After completion of the dropping of the liquid mixture and dimethyldimethoxysilane into the reactor, the temperature in the reactor was elevated to 85 °C and the mixture was allowed to stand for 6 hours. After cooling the mixture in the reactor to room temperature, the hydrogen ion concentration thereof was measured to give a pH value of 2.1. A 25 % aqueous solution of ammonia was added to the mixture in the reactor to thereby adjust the pH value thereof to 8. Then, the resultant mixture was filtered by means of a 100-mesh metal wire net to thereby obtain a final aqueous, silicone-modified acrylate polymer emulsion. The amount of filtered-off aggregates was as small as 0.02 % by weight (on a dry basis), based on the total weight of the monomers. With respect to the obtained emulsion, the solids content of the emulsion was 43.5 %, and the average particle diameter of the dispersed phase of the emulsion was 980 Å. Using this emulsion, a paint was prepared, and the paint thus prepared was examined with respect to the initial gloss value, gloss retentivity and water resistance. Results are shown in Table 1.

Comparative Example 4

[0074] 300 Parts of water, 52 parts of methyl methacrylate, 40 parts of butyl acrylate, 8 parts of methacrylic acid and 20 parts of a 20 % aqueous solution of Latemul S-180A (ammonium salt of diester of sulfosuccinic acid, which has a

double bond and is copolymerizable with an ethylenically unsaturated monomer) (manufactured and sold by Kao Corp., Japan) were charged in a reactor having a stirrer, a reflux condenser, dropping tanks and a thermometer. After elevating the temperature in the reactor to 78 °C, 0.5 part of ammonium persulfate was added to the reactor, and the resultant mixture was allowed to stand for 1 hour, thereby obtaining a preliminary aqueous acrylate polymer emulsion having a seed latex dispersed therein. The hydrogen ion concentration of the obtained preliminary aqueous acrylate polymer emulsion was measured to give a pH value of 1.8. Then, a liquid mixture of 330 parts of water, 207 parts of methyl methacrylate, 190 parts of butyl acrylate, 3 parts of methacrylic acid, 20 parts of a 20 % aqueous solution of Latemul S-180A and 1.0 part of ammonium persulfate was dropped into the reactor from a dropping tank over 3 hours. During the dropping of the above-mentioned liquid mixture into the reactor, the temperature in the reactor was maintained at 80 °C. After completion of the dropping of the liquid mixture into the reactor, the temperature in the reactor was elevated to 85 °C and the mixture was allowed to stand for 6 hours. After cooling the mixture in the reactor to room temperature, the hydrogen ion concentration thereof was measured to give a pH value of 2.1. A 25 % aqueous solution of ammonia was added to the mixture in the reactor to thereby adjust the pH value thereof to 8. Then, the resultant mixture was filtered by means of a 100-mesh metal wire net to thereby obtain a final emulsion. The amount of filtered-off aggregates was as small as 0.02 % by weight (on a dry basis), based on the total weight of the monomers. With respect to the obtained emulsion, the solids content of the emulsion was 43.0 %, and the average particle diameter of the dispersed phase of the emulsion was 1080 Å. Using this emulsion, a paint was prepared, and the paint thus prepared was examined with respect to the initial gloss value, gloss retentivity and water resistance. Results are shown in Table 1.

Example 2

[0075] 300 Parts of water, 37 parts of methyl methacrylate, 40 parts of n-butyl acrylate, 15 parts of cyclohexyl methacrylate, 8 parts of methacrylic acid and 20 parts of a 20 % aqueous solution of Latemul S-180A (ammonium salt of diester of sulfosuccinic acid, which has a double bond and is copolymerizable with an ethylenically unsaturated monomer) (manufactured and sold by Kao Corp., Japan) were charged in a reactor having a stirrer, a reflux condenser, dropping tanks and a thermometer. After elevating the temperature in the reactor to 78 °C, 0.5 part of ammonium persulfate was added to the reactor, and the resultant mixture was allowed to stand for 1 hour, thereby obtaining a preliminary aqueous acrylate polymer emulsion having a seed latex dispersed therein. The hydrogen ion concentration of the obtained preliminary aqueous acrylate polymer emulsion was measured to give a pH value of 1.9. Then, a liquid mixture of 2.5 parts of γ -methacryloxypropyltrimethoxysilane, 25 parts of dimethyldimethoxysilane and 25 parts of methyltrimethoxysilane was dropped into the reactor from a dropping tank over 5 minutes. Subsequently, a liquid mixture of 330 parts of water, 180 parts of methyl methacrylate, 160 parts of butyl acrylate, 60 parts of cyclohexyl methacrylate, 20 parts of a 20 % aqueous solution of Latemul S-180A and 1.0 part of ammonium persulfate was dropped into the reactor from another dropping tank over 3 hours. During the dropping of the above-mentioned liquid mixtures into the reactor, the temperature in the reactor was maintained at 80 °C.

[0076] After completion of the dropping of the liquid mixtures into the reactor, the temperature in the reactor was elevated to 85 °C and the mixture was allowed to stand for 6 hours. After cooling the mixture in the reactor to room temperature, the hydrogen ion concentration thereof was measured to obtain a pH value of 2.1. A 25 % aqueous solution of ammonia was added to the mixture in the reactor to thereby adjust the pH value thereof to 8. Then, the resultant mixture was filtered by means of a 100-mesh metal wire net to thereby obtain a final aqueous, silicone-modified acrylate polymer emulsion. The amount of filtered-off aggregates was as small as 0.02 % by weight (on a dry basis), based on the total weight of the monomers. With respect to the obtained emulsion, the solids content of the emulsion was 44.0 %, and the average particle diameter of the dispersed phase of the emulsion was 970 Å. Using this emulsion, a paint was prepared, and the paint thus prepared was examined with respect to the initial gloss value, gloss retentivity and water resistance. Results are shown in Table 1.

Example 3

[0077] 400 Parts of water, 122 parts of n-butyl methacrylate, 60 parts of methyl methacrylate, 18 parts of methacrylic acid and 30 parts of a 20 % aqueous solution of Latemul S-180A were charged in a reactor having a stirrer, a reflux condenser, dropping tanks and a thermometer. After elevating the temperature in the reactor to 78 °C, 1.0 part of ammonium persulfate was added to the reactor, and the resultant mixture was allowed to stand for 1 hour, thereby obtaining a preliminary aqueous acrylate polymer emulsion having a seed latex dispersed therein. The hydrogen ion concentration of the obtained preliminary aqueous acrylate polymer emulsion was measured to give a pH value of 1.7. Then, a liquid mixture of 50 parts of dimethyldimethoxysilane and 50 parts of methyltrimethoxysilane was dropped into the reactor from a dropping tank over 5 minutes, while maintaining the temperature in the reactor at 60 °C and the resultant mixture was allowed to stand at 80 °C for 2 hours. Subsequently, a liquid mixture of 230 parts of water, 140 parts of n-butyl methacrylate, 150 parts of cyclohexyl methacrylate, 10 parts of methacrylic acid, 18 parts of a 20 %

aqueous solution of sodium p-styrenesulfonate, 2 parts of a 20 % aqueous solution of sodium dodecylbenzenesulfonate and 1.0 part of ammonium persulfate, and 2.5 parts of γ -methacryloxypropyltrimethoxysilane were individually dropped into the reactor from separate dropping tanks over 3 hours. During the dropping of the above-mentioned liquid mixtures into the reactor, the temperature in the reactor was maintained at 80 °C. After completion of the dropping of the liquid mixtures into the reactor, the temperature in the reactor was elevated to 85 °C and the mixture was allowed to stand for 6 hours. After cooling the mixture in the reactor to room temperature, the hydrogen ion concentration thereof was measured to give a pH value of 2.0. A 25 % aqueous solution of ammonia was added to the mixture in the reactor to thereby adjust the pH value thereof to 8. Then, the resultant mixture was filtered by means of a 100-mesh metal wire net to thereby obtain a final aqueous, silicone-modified acrylate polymer emulsion. The amount of filtered-off aggregates was as small as 0.02 % by weight (on a dry basis), based on the total weight of the monomers. With respect to the obtained emulsion, the solids content of the emulsion was 45.4 %, and the average particle diameter of the dispersed phase of the emulsion was 1020 Å. Using this emulsion, a paint was prepared, and the paint thus prepared was examined with respect to the initial gloss value, gloss retentivity and water resistance. Results are shown in Table 1.

Example 4

[0078] 300 Parts of water, 40 parts of cyclohexyl acrylate, 15 parts of 2-hydroxycyclohexyl methacrylate, 30 parts of 2-ethylhexyl acrylate, 15 parts of acrylic acid and 20 parts of a 25 % aqueous solution of Adeca Rea soap SE-1025N (manufactured and sold by ASahi DENKA KOGYO K.K., Japan) were charged in a reactor having a stirrer, a reflux condenser, dropping tanks and a thermometer. After elevating the temperature in the reactor to 78 °C, 0.5 part of ammonium persulfate was added to the reactor, and the resultant mixture was allowed to stand for 1 hour, thereby obtaining a preliminary aqueous acrylate polymer emulsion having a seed latex dispersed therein. The hydrogen ion concentration of the obtained preliminary aqueous acrylate polymer emulsion was measured to give a pH value of 1.8. Then, a liquid mixture of 25 parts of dimethyldimethoxysilane and 25 parts of methyltrimethoxysilane was dropped into the reactor from a dropping tank over 5 minutes, while maintaining the temperature in the reactor at 60 °C, and the resultant mixture was allowed to stand at 80 °C for 2 hours. Subsequently, a liquid mixture of 330 parts of water, 280 parts of cyclohexyl acrylate, 120 parts of 2-ethylhexyl acrylate, 18 parts of 25 % aqueous solution of Adeca Rea soap SE-1025N, 2 parts of a 20 % aqueous solution of sodium dodecylbenzenesulfonate and 1.0 part of ammonium persulfate, and 2.5 parts of γ -methacryloxypropyltrimethoxysilane were individually dropped into the reactor from separate dropping tanks over 3 hours. During the dropping of the above-mentioned liquid mixtures into the reactor, the temperature in the reactor was maintained at 80 °C. After completion of the dropping of the liquid mixtures into the reactor, the temperature in the reactor was elevated to 85 °C and the mixture was allowed to stand for 6 hours. After cooling the mixture in the reactor to room temperature, the hydrogen ion concentration thereof was measured to give a pH value of 2.0. A 25 % aqueous solution of ammonia was added to the mixture in the reactor to thereby adjust the pH value thereof to 8. Then, the resultant mixture was filtered by means of a 100-mesh metal wire net to thereby obtain a final aqueous, silicone-modified acrylate polymer emulsion. The amount of filtered-off aggregates was as small as 0.02 % by weight (on a dry basis), based on the total weight of the monomers. With respect to the obtained emulsion, the solids content of the emulsion was 44.0 %, and the average particle diameter of the dispersed phase of the emulsion was 1190 Å. Using this emulsion, a paint was prepared, and the paint thus prepared was examined with respect to the initial gloss value, gloss retentivity and water resistance. Results are shown in Table 1.

Comparative Examples 5 through 9

(1) Preparation of a preliminary aqueous acrylate polymer emulsion having a seed latex dispersed therein

[0079] 381.5 Parts of water, 40 parts of butyl acrylate, 40 parts of methyl methacrylate, 5 parts of itaconic acid, 10 parts of methacrylic acid, 5 parts of styrene and 18 parts of a 25 % aqueous solution of Aquaron HS-10 (ammonium salt of sulfuric acid ester of polyoxyethylene alkylphenyl ether, which has a double bond and is copolymerizable with an ethylenically unsaturated monomer) (manufactured and sold by Dai-ichi Kogyo Sanyaku Co., Ltd., Japan) were charged in a reactor having a stirrer, a reflux condenser, dropping tanks and a thermometer. After elevating the temperature in the reactor to 78 °C, 0.5 part of ammonium persulfate was added to the reactor, and the resultant mixture was allowed to stand for 1 hour, thereby obtaining a preliminary aqueous acrylate polymer emulsion having a seed latex dispersed therein. The hydrogen ion concentration of the obtained preliminary aqueous acrylate polymer emulsion was measured to give a pH value of 1.7.

(2) Preparation of emulsions (a) to (e)

[0080] In each of Examples 6 through 10, a liquid mixture of a predetermined amount (Indicated in Table 2) of the

above-obtained preliminary aqueous acrylate polymer emulsion (having a seed latex dispersed therein), 80 parts of a 25 % aqueous solution of Aquaron HS-10 as an emulsifier, 5.0 parts of ammonium persulfate, 655 parts of water and monomers indicated in Table 2 as monomer system (A), and hydrolyzable silanes indicated in Table 2 were individually dropped into the reactor from two separate dropping tanks over 3 hours. During the dropping of the above-mentioned liquid mixtures into the reactor, the temperature in the reactor was maintained at 80 °C. After completion of the dropping of the liquid mixtures into the reactor, the temperature in the reactor was elevated to 85 °C and the mixture was allowed to stand for 6 hours. After cooling the mixture in the reactor to room temperature, the hydrogen ion concentration thereof in each Example was individually measured to obtain a respective pH value which was in the range of from 1.5 to 2.5. A 25 % aqueous solution of ammonia was added to the mixture in the reactor to thereby adjust the pH value thereof to 8. Then, the resultant mixture was filtered by means of a 100-mesh metal wire net to thereby obtain a final aqueous, silicone-modified acrylate polymer emulsion. With respect to each of the emulsions obtained in Examples 6 through 10, the amount of filtered-off aggregates was as small as 0.5 % by weight or less (on a dry basis), based on the total weight of the monomers. Using these emulsions, paints were prepared, respectively, and the paints thus prepared were examined with respect to the initial gloss value, gloss retentivity and water resistance. Results are shown in Table 2.

(3) Results of the examination

[0081] Emulsions (a) to (e) obtained respectively in Examples 6 to 10 exhibited excellent initial gloss value, gloss retentivity and water resistance.

Table 1

	Examples				Comparative Examples			
	1	2	3	4	1	2	3	4
Initial gloss value (%)	84	82	84	80	81	79	65	80
Gloss retentivity (%)	98	95	96	91	80	85	60	48
Water resistance	⊙	⊙	⊙	⊙	⊙	×	⊙	⊙

[0082] Criterion for evaluation of water resistance

- ⊙ : No blistering or lowering of luster is observed.
- : Slight blistering is observed, but no lowering of luster is observed.*
- Δ : Blistering and lowering of luster are observed.*
- ×

Table 2

Comparative Examples					5	6	7	8	9
Emulsions					a	b	c	d	e
Preliminary aqueous acrylate polymer emulsion having a seed latex dispersed therein (parts by weight)					1000	1000	1000	200	200
[Monomers used as a monomer system (A)] (parts by weight)									
n-butyl acrylate					390	390	390	350	350
2-ethylhexyl acrylate					590	590	590	585	350
Methyl methacrylate									585
Styrene					20	20	20	50	50
Methacrylic acid								15	15
[Aqueous solution containing monomers used as an emulsifier (B)] (parts by weight)									
25% aqueous solution of Aquaron HS-10					80	80	80	80	80

* Among the paints prepared in Examples and Comparative Examples, no paints were found which were evaluated as ○ or Δ.

Table 2 (continued)

Comparative Examples	5	6	7	8	9
[Hydrolyzable silanes used as a modifier (C)] (parts by weight)					
γ -methacryloxypropyltrimethoxysilane	100	45	45	5	5
Methyltriethoxysilane				50	50
Dimethyldiethoxysilane		100	50	200	50
Octamethylcyclotetrasiloxane					
[Examination items]					
Initial gloss value (%)	79	82	78	76	77
Gloss retentivity (%)	80	85	85	91	76
Water resistance	⊙	⊙	⊙	⊙	⊙

INDUSTRIAL APPLICABILITY

[0083] The aqueous, silicone-modified acrylate polymer emulsion of the present invention is capable of forming such an excellent coating as has not conventionally been achieved, i.e., a coating having excellent water repellency, water resistance, weatherability, dispersion characteristics of pigment, gloss retentivity, stain resistance and adhesion properties. Therefore, the aqueous, silicone-modified acrylate polymer emulsion of the present invention can be advantageously used as a paint, an undercoating or finish coating material for building materials, an adhesive, a pressure-sensitive adhesive, a processing agent for papers, or a finish coating material for textile fabrics. Especially, the aqueous, silicone-modified acrylate polymer emulsion of the present invention can be advantageously used as a paint, or a finish coating material for building materials.

Claims

1. An aqueous, silicone-modified acrylate polymer emulsion, which is an acrylate polymer emulsion produced by subjecting a monomer system (A) to emulsion polymerization in an aqueous medium in the presence of an emulsifier (B), wherein said acrylate polymer emulsion is silicone-modified using a silicone structure-containing modifier (C) during or after said emulsion polymerization;

wherein said monomer system (A) comprises an acrylate monomer selected from the group consisting of an acrylic ester, a methacrylic ester and a mixture thereof, said acrylate monomer containing 5 % by weight or more, based on the weight of said monomer system (A), of a C₅-C₁₂ cycloalkyl ester of acrylic acid, a C₅-C₁₂ cycloalkyl ester of methacrylic acid, or a mixture thereof;

wherein said emulsifier (B) is selected from the group consisting of a sulfonic acid group-containing ethylenically unsaturated monomer, a sulfonate group-containing ethylenically unsaturated monomer, and a mixture thereof; and

wherein said silicone structure-containing modifier (C) comprises at least one silicone structure-containing silane (I) represented by the formula:



wherein R¹ represents a hydrogen atom, a C₁-C₁₆ aliphatic hydrocarbon group, a C₅-C₁₀ aryl group, a C₅-C₆ cycloalkyl group, a vinyl group, an acrylic C₁-C₁₀ alkyl group or a methacrylic C₁-C₁₀ alkyl group, and each R² independently represents a C₁-C₈ alkoxy group, an acetoxy group or a hydroxyl group and at least one member selected from the group consisting of a cyclic silane and a silane (III) represented by the formula:



wherein each R³ independently represents a hydrogen atom, a C₁-C₁₆ aliphatic hydrocarbon group, a C₅-C₁₀ aryl group, a C₅-C₆ cycloalkyl group, a vinyl group, an acrylic C₁-C₁₀ alkyl group or a methacrylic C₁-C₁₀ alkyl

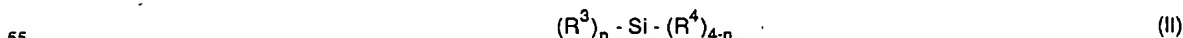
group, and each R⁴ independently represents a C₁-C₈ alkoxy group, an acetoxy group or a hydroxyl group; and wherein the molar ratio of said silane (I) to said at least one member selected from the group consisting of a cyclic silane and a silane (III) is at least 10/100.

- 5 2. The aqueous, silicone-modified acrylate polymer emulsion according to claim 1, wherein said monomer system (A) and said emulsifier (B) are, respectively, used in an amount of from 80 to 99.95% by weight and in an amount of from 0.05 to 20% by weight, based on the total weight of monomer system (A) and emulsifier (B), and said silicone structure-containing modifier (C) is used in an amount which satisfies the following relationships:

$$10 \quad \frac{1}{2} \frac{(A) + (B)}{(C)} \frac{99}{1}$$

wherein (A), (B) and (C), respectively, represent amounts of monomer system (A), emulsifier (B) and modifier (C) in terms of weight percentages based on the total weight of materials (A), (B) and (C).

- 15 3. The aqueous, silicone-modified acrylate polymer emulsion according to claim 1 or 2, wherein the ratio of the total weight of said monomer system (A), said emulsifier (B) and said modifier (C) to the weight of said aqueous medium is 75/25 or less.
- 20 4. The aqueous, silicone-modified acrylate polymer emulsion according to claim 1, wherein said monomer system (A) further comprises a comonomer copolymerizable with said acrylate monomer, said comonomer being at least one member selected from the group consisting of an acrylamide monomer, a methacrylamide monomer, a vinyl monomer and a carboxylic acid group-containing ethylenically unsaturated monomer, and wherein said acrylate monomer and said comonomer are, respectively, present in an amount of from 90% to less than 100% by weight and in an amount of from 10% by weight or less, based on the total weight of said acrylate monomer and said comonomer.
- 25 5. The aqueous, silicone-modified acrylate polymer emulsion according to claim 4, wherein said comonomer of said monomer system (A) is a carboxylic acid group-containing ethylenically unsaturated monomer.
- 30 6. The aqueous, silicone-modified acrylate polymer emulsion according to claim 5, wherein said carboxylic acid group-containing ethylenically unsaturated monomer is at least one member selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid and a half ester thereof, fumaric acid and a half ester thereof, and maleic acid and a half ester thereof.
- 35 7. The aqueous, silicone-modified acrylate polymer emulsion according to claim 1, wherein said sulfonic acid group-containing ethylenically unsaturated monomer or said sulfonate group-containing ethylenically unsaturated monomer of said emulsifier (B) is a radically polymerizable double bond-containing compound having a sulfonic acid group, or an ammonium or an alkali metal salt thereof.
- 40 8. The aqueous, silicone-modified acrylate polymer emulsion according to claim 7, wherein said sulfonic acid group-containing ethylenically unsaturated monomer or said sulfonate group-containing ethylenically unsaturated monomer of said emulsifier (B) is a radically polymerizable double bond-containing compound having a substituent selected from the group consisting of a C₁-C₂₀ alkyl group, a C₂-C₄ alkyl ether group, a poly-C₂-C₄ alkyl ether group, a C₆ or C₁₀ aryl group, and a succinic acid group, each of which is substituted with a sulfonic acid group which is in the form of an ammonium, a sodium or a potassium salt thereof, or a vinyl sulfonate compound having a vinyl group bonded to a sulfonic acid group which is in the form of an ammonium, a sodium or a potassium salt thereof.
- 45 9. The aqueous, silicone-modified acrylate polymer emulsion according to claim 1, wherein said silicone structure-containing modifier (C) further comprises at least one member selected from the group consisting of a hydrolyzable group-containing linear siloxane and a silane (II) represented by the formula:



wherein each R³ independently represents a hydrogen atom, a C₁-C₁₆ aliphatic hydrocarbon group, a C₅-C₁₀

aryl group, a C₅-C₆ cycloalkyl group, a vinyl group, an acrylic C₁-C₁₀ alkyl group or a methacrylic C₁-C₁₀ alkyl group, each R⁴ independently represents a C₁-C₈ alkoxy group, an acetoxy group or a hydroxyl group, and n is 0 or 3; and

wherein the molar ratio of said silane (I) to the total of said at least one member selected from the group consisting of the cyclic silane and the silane (III), and said at least one member selected from the group consisting of hydrolyzable group-containing linear siloxane and the silane (II) is at least 10/100.

10. The aqueous, silicone-modified acrylate polymer emulsion according to claim 1, wherein said modifier (C) is added to a system of said emulsion polymerization, so that the silicone-modification of said emulsion is performed during said emulsion polymerization.

11. The aqueous, silicone-modified acrylate polymer emulsion according to claim 1, wherein said monomer system (A) is comprised of monomer systems (A¹) and (A²), each comprising said acrylate monomer, and said emulsifier (B) is comprised of emulsifiers (B¹) and (B²), each selected from the group consisting of said sulfonic acid group-containing ethylenically unsaturated monomer, said sulfonate group-containing ethylenically unsaturated monomer, and said mixture thereof, with the proviso that monomer systems (A¹) and (A²) are the same or different, and emulsifiers (B¹) and (B²) are the same or different, and wherein said emulsion polymerization is conducted in a sequence of step (1) and step (2), wherein in step (1), said monomer system (A¹) is subjected to emulsion polymerization in an aqueous medium in the presence of said emulsifier (B¹) to thereby obtain a preliminary aqueous acrylate polymer emulsion having a seed latex dispersed therein, and in step (2), said monomer system (A²) and said emulsifier (B²), optionally with an aqueous medium, are added to said preliminary aqueous acrylate polymer emulsion to effect emulsion polymerization thereof, thereby producing a final aqueous acrylate polymer emulsion, wherein said silicone-modification is performed using said silicone structure-containing modifier (C) during or after said emulsion polymerization.

12. The aqueous, silicone-modified acrylate polymer emulsion according to claim 11, wherein said modifier (C) is added in step (2) to perform the silicone-modification during the emulsion polymerization.

13. The aqueous, silicone-modified acrylate polymer emulsion according to claim 11, wherein said final aqueous acrylate emulsion is treated with said modifier (C) to perform said silicone-modification after said emulsion polymerization.

14. The aqueous, silicone-modified acrylate polymer emulsion according to claim 11, wherein in step (1), said monomer system (A¹) and said emulsifier (B¹) are, respectively, used in an amount of from 80 to 99.95% by weight and in an amount of from 20 to 0.05% by weight, based on the total weight of monomer system (A¹) and emulsifier (B¹); and wherein in step (2), said monomer system (A²) and said emulsifier (B²) are, respectively, used in an amount of from 80 to 99.95% by weight and in an amount of from 20 to 0.05% by weight, based on the total weight of monomer system (A²) and emulsifier (B²),

wherein said silicone structure-containing modifier (C) is used in an amount which satisfies the following relationships:

$$\frac{1}{2} \frac{(A^1) + (A^2) + (B^1) + (B^2)}{(C)} \frac{99}{1}$$

wherein (A¹), (A²), (B¹), (B²) and (C), respectively, represent amounts of monomer system (A¹), monomer system (A²), emulsifier (B¹), emulsifier (B²) and modifier (C) in terms of weight percentages based on the total weight of materials (A¹), (A²), (B¹), (B²) and (C), and

wherein the ratio of the total weight of said monomer system (A¹) and emulsifier (B¹) to the total weight of said monomer system (A²) and emulsifier (B²) is from 1/99 to 99/1.

15. The aqueous, silicone-modified acrylate polymer emulsion according to claim 14, wherein in step (1), said monomer system (A¹) contains 0.5 to 30% by weight of a carboxylic acid group-containing ethylenically unsaturated monomer, based on the weight of said monomer system (A¹).

16. The aqueous, silicone-modified acrylate polymer emulsion according to any one of claims 1 to 15, which is a paint, an undercoating or finish coating material for building materials, an adhesive, a pressure-sensitive adhesive, a processing agent for papers, or a finish coating material for textile fabrics.

17. The aqueous, silicone-modified acrylate polymer emulsion according to claim 16, which is a paint, or a finish coating material for building materials.

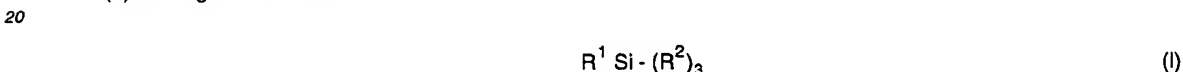
5 Patentansprüche

1. Wässrige Emulsion eines silikonmodifizierten Acrylatpolymers, welche eine Acrylatpolymeremulsion, erhalten durch Emulsionspolymerisation eines Monomersystems (A) in einem wässrigen Medium in Anwesenheit eines Emulgiermittels (B), ist, wobei die Acrylatpolymeremulsion unter Einsatz eines Silikonstruktur enthaltenden Modifiziermittels (C) während oder nach der Emulsionspolymerisation mit Silikon modifiziert wird;

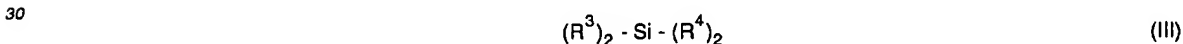
wobei das Monomersystem (A) ein Acrylatmonomer enthält, das aus der Gruppe ausgewählt ist, die aus einem Acrylsäureester, einem Methacrylsäureester und einem Gemisch davon besteht, wobei das Acrylatmonomer mindestens 5 Gew.-%, bezogen auf das Gewicht des Monomersystems (A), eines C₅-C₁₂-Cycloalkylesters von Acrylsäure, eines C₅-C₁₂-Cycloalkylesters von Methacrylsäure oder eines Gemisches davon enthält;

wobei das Emulgiermittel (B) aus der Gruppe ausgewählt ist, die aus Sulfonsäuregruppe enthaltendem ethylenisch ungesättigten Monomer, Sulfonatgruppe enthaltendem ethylenisch ungesättigten Monomer und einem Gemisch davon besteht; und

wobei das Silikonstruktur enthaltende Modifiziermittel (C) mindestens ein Silikonstruktur enthaltendes Silan (I) der folgenden Formel:



worin R¹ ein Wasserstoffatom, eine C₁-C₁₆ aliphatische Kohlenwasserstoffgruppe, eine C₅-C₁₀-Arylgruppe, eine C₅-C₆-Cycloalkylgruppe, eine Vinylgruppe, eine acrylische C₁-C₁₀-Alkylgruppe oder eine methacrylische C₁-C₁₀-Alkylgruppe darstellt und R² jeweils unabhängig voneinander eine C₁-C₈-Alkoxygruppe, eine Acetoxygruppe oder eine Hydroxygruppe darstellen, und mindestens ein Mitglied enthält, das aus der Gruppe ausgewählt ist, die aus einem cyclischen Silan und einem Silan (III) der folgenden Formel besteht:



worin R³ jeweils unabhängig voneinander ein Wasserstoffatom, eine aliphatische C₁-C₁₆-Kohlenwasserstoffgruppe, eine C₅-C₁₀-Arylgruppe, eine C₅-C₆-Cycloalkylgruppe, eine Vinylgruppe, eine acrylische C₁-C₁₀-Alkylgruppe oder eine methacrylische C₁-C₁₀-Alkylgruppe darstellt und R⁴ jeweils unabhängig voneinander eine C₁-C₈-Alkoxygruppe, eine Acetoxygruppe oder eine Hydroxygruppe darstellen;

worin das Molverhältnis des Silans (I) zu dem mindestens einen Mitglied, das aus der aus einem cyclischen Silan und einem Silan (III) bestehenden Gruppe ausgewählt ist, mindestens 10/100 ist.

2. Wässrige Emulsion eines silikonmodifizierten Acrylatpolymers nach Anspruch 1, worin das Monomersystem (A) und das Emulgiermittel (B) in einer Menge von 80 bis 99,95 Gew.-% bzw. in einer Menge von 0,05 bis 20 Gew.-%, bezogen auf das Gesamtgewicht des Monomersystems (A) und des Emulgiermittels (B), eingesetzt wird und das Silikonstruktur enthaltende Modifiziermittel (C) in einer Menge eingesetzt wird, welche die folgende Beziehung erfüllt:

$$\frac{1}{2} \leq \frac{(A) + (B)}{(C)} \leq \frac{99}{1}$$

worin (A), (B) bzw. (C) die Menge des Monomersystems (A), des Emulgiermittels (B) bzw. des Modifiziermittels (C), ausgedrückt als Gewichtsprozent, bezogen auf das Gesamtgewicht der Materialien (A), (B) und (C), darstellt.

3. Wässrige Emulsion eines silikonmodifizierten Acrylatpolymers nach Anspruch 1 oder 2, worin das Verhältnis des Gesamtgewichts des Monomersystems (A), des Emulgiermittels (B) und des Modifiziermittels (C) zu dem Gewicht des wässrigen Mediums 75/25 oder weniger ist.

4. Wässrige Emulsion eines silikonmodifizierten Acrylatpolymers nach Anspruch 1, worin das Monomersystem (A)

außerdem ein Comonomer enthält, das mit dem Acrylatmonomer copolymerisierbar ist, wobei das Comonomer mindestens ein Mitglied ist, das aus der Gruppe ausgewählt ist, die aus einem Acrylamidmonomer, einem Methacrylamidmonomer, einem Vinylmonomer und einem Carbonsäuregruppe enthaltenden ethylenisch ungesättigten Monomer besteht, und worin das Acrylatmonomer bzw. das Comonomer in einer Menge von 90 bis höchstens 100 Gew.-% bzw. in einer Menge von höchstens 10 Gew.-%, bezogen auf das Gesamtgewicht des Acrylatmonomers und des Comonomers, vorhanden ist.

5. Wässrige Emulsion eines silikonmodifizierten Acrylatpolymers nach Anspruch 4, worin das Comonomer des Monomersystems (A) ein Carbonsäuregruppe enthaltendes ethylenisch ungesättigtes Monomer ist.

6. Wässrige Emulsion eines silikonmodifizierten Acrylatpolymers nach Anspruch 5, worin das Carbonsäuregruppe enthaltende ethylenisch ungesättigte Monomer mindestens ein Mitglied ist, das aus der Gruppe ausgewählt ist, die aus Acrylsäure, Methacrylsäure, Itaconsäure und einem Halbester davon, Fumarsäure und einem Halbester davon, und Maleinsäure und einem Halbester davon besteht.

7. Wässrige Emulsion eines silikonmodifizierten Acrylatpolymers nach Anspruch 1, worin das Sulfonsäuregruppe enthaltende ethylenisch ungesättigte Monomer oder das Sulfonatgruppe enthaltende ethylenisch ungesättigte Monomer des Emulgiermittels (B) eine radikalisch polymerisierbare, Doppelbindung enthaltende Verbindung mit einer Sulfonsäuregruppe oder einem Ammonium- oder Alkalimetallsalz davon ist.

8. Wässrige Emulsion eines silikonmodifizierten Acrylatpolymers nach Anspruch 7, worin das Sulfonsäuregruppe enthaltende ethylenisch ungesättigte Monomer oder das Sulfonatgruppe enthaltende ethylenisch ungesättigte Monomer des Emulgiermittels (B) eine radikalisch polymerisierbare, Doppelbindung enthaltende Verbindung mit einem Substituenten, der aus der Gruppe ausgewählt ist, die aus einer C₁-C₂₀-Alkylgruppe, einer C₂-C₄-Alkylethergruppe, einer Poly-C₂-C₄-Alkylethergruppe, einer C₆- oder C₁₀-Arylgruppe und einer Bernsteinsäuregruppe besteht, wobei jeder Substituent mit einer Sulfonsäuregruppe substituiert ist, die in der Form eines Ammonium-, Natrium- oder Kaliumsalzes davon vorliegt, oder eine Vinylsulfonatverbindung mit einer Vinylgruppe ist, die an eine in der Form eines Ammonium-, Natrium- oder Kaliumsalzes vorliegenden Sulfonsäuregruppe gebunden ist.

9. Wässrige Emulsion eines silikonmodifizierten Acrylatpolymers nach Anspruch 1, worin das Silikonstruktur enthaltende Modifizierungsmittel (C) außerdem mindestens ein Mitglied enthält, das aus der Gruppe ausgewählt ist, die aus einem hydrolysierbaren Gruppe enthaltenden linearen Siloxan und einem Silan (II) der folgenden Formel besteht:



worin R³ jeweils unabhängig voneinander ein Wasserstoffatom, eine aliphatische C₁-C₁₆-Kohlenwasserstoffgruppe, eine C₅-C₁₀-Arylgruppe, eine C₅-C₆-Cycloalkylgruppe, eine Vinylgruppe, eine acrylische C₁-C₁₀-Alkylgruppe oder eine methacrylische C₁-C₁₀-Alkylgruppe darstellen, wobei R⁴ jeweils unabhängig voneinander eine C₁-C₈-Alkoxygruppe, eine Acetoxygruppe oder eine Hydroxygruppe darstellen und n 0 oder 3 ist;

worin das Molverhältnis des Silans (I) zur Summe des mindestens einen Mitglieds, das aus der aus dem cyclischen Silan und dem Silan (III) bestehenden Gruppe ausgewählt ist, und dem mindestens einen Mitglied, das aus der aus hydrolysierbaren Gruppe enthaltendem linearen Siloxan und dem Silan (II) bestehenden Gruppe ausgewählt ist, mindestens 10/100 ist.

10. Wässrige Emulsion eines silikonmodifizierten Acrylatpolymers nach Anspruch 1, worin das Modifizierungsmittel (C) zu dem System der Emulsionspolymerisation gegeben wird, so daß die Silikonmodifizierung der Emulsion während der Emulsionspolymerisation durchgeführt wird.

11. Wässrige Emulsion eines silikonmodifizierten Acrylatpolymers nach Anspruch 1, worin das Monomersystem (A) aus Monomersystemen (A¹) und (A²), die jeweils das Acrylatmonomer enthalten, besteht, und das Emulgiermittel (B) aus Emulgiermitteln (B¹) und (B²) besteht, die jeweils aus der Gruppe ausgewählt sind, die aus dem Sulfonsäure enthaltenden ethylenisch ungesättigten Monomer, dem Sulfonatgruppe enthaltenden ethylenisch ungesättigten Monomer und dem Gemisch davon besteht, mit der Maßgabe, daß die Monomersysteme (A¹) und (A²) gleich oder unterschiedlich sind und die Emulgiermittel (B¹) und (B²) gleich oder unterschiedlich sind, und worin die Emulsionspolymerisation in der Reihenfolge Stufe (1) und Stufe (2) durchgeführt wird, wobei in Stufe (1)

das Monomersystem (A¹) einer Emulsionspolymerisation in einem wässrigen Medium in Anwesenheit des Emulgiermittels (B¹) unterworfen wird, um eine vorläufige wässrige Acrylatpolymeremulsion zu erhalten, die einen darin dispergierten Latexkeim enthält, und in Stufe (2) das Monomersystem (A²) und das Emulgiermittel (B²) gegebenenfalls mit einem wässrigen Medium zu der vorläufigen wässrigen Acrylatpolymeremulsion gegeben werden, um die Emulsionspolymerisation zu bewirken, wodurch die endgültige wässrige Acrylatpolymeremulsion erhalten wird, wobei die Silikonmodifikation unter Einsatz des Silikonstruktur enthaltenden Modifiziermittels (C) während oder nach der Emulsionspolymerisation durchgeführt wird.

12. Wässrige Emulsion eines silikonmodifizierten Acrylatpolymers nach Anspruch 11, worin das Modifiziermittel (C) in Stufe (2) zugegeben wird, um die Silikonmodifikation während der Emulsionspolymerisation durchzuführen.

13. Wässrige Emulsion eines silikonmodifizierten Acrylatpolymers nach Anspruch 11, worin die endgültige wässrige Acrylatemulsion mit dem Modifiziermittel (C) behandelt wird, um die Silikonmodifikation nach der Emulsionspolymerisation durchzuführen.

14. Wässrige Emulsion eines silikonmodifizierten Acrylatpolymers nach Anspruch 11, worin in Stufe (1) das Monomersystem (A¹) bzw. das Emulgiermittel (B¹) in einer Menge von 80 bis 99,95 Gew.-% bzw. in einer Menge von 20 bis 0,05 Gew.-%, bezogen auf das Gesamtgewicht des Monomersystems (A¹) und des Emulgiermittels (B¹), eingesetzt wird; und worin in Stufe (2) das Monomersystem (A²) bzw. das Emulgiermittel (B²) in einer Menge von 80 bis 99,95 Gew.-% bzw. in einer Menge von 20 bis 0,05 Gew.-%, bezogen auf das Gesamtgewicht des Monomersystems (A²) und des Emulgiermittels (B²), eingesetzt wird,

worin das Silikonstruktur enthaltende Modifiziermittel (C) in einer Menge eingesetzt wird, welche die folgende Beziehung erfüllt:

$$\frac{1}{2} \leq \frac{(A^1) + (A^2) + (B^1) + (B^2)}{(C)} \leq \frac{99}{1}$$

worin (A¹), (A²), (B¹), (B²) bzw. (C) die Menge des Monomersystems (A¹), des Monomersystems (A²), des Emulgiermittels (B¹), des Emulgiermittels (B²) und des Modifiziermittels (C), ausgedrückt als Gewichtsprozent, bezogen auf das Gesamtgewicht der Materialien (A¹), (A²), (B¹), (B²) und (C), darstellt, und

worin das Verhältnis des Gesamtgewichts des Monomersystems (A¹) und des Emulgiermittels (B¹) zu dem Gesamtgewicht des Monomersystems (A²) und des Emulgiermittels (B²) 1/99 bis 99/1 ist.

15. Wässrige Emulsion eines silikonmodifizierten Acrylatpolymers nach Anspruch 14, worin in Stufe (1) das Monomersystem (A¹) 0,5 bis 30 Gew.-% eines Carbonsäuregruppe enthaltenden ethylenisch ungesättigten Monomers, bezogen auf das Gewicht des Monomersystems (A¹), enthält.

16. Wässrige Emulsion eines silikonmodifizierten Acrylatpolymers nach einem der Ansprüche 1 bis 15, welche eine Farbe, ein Grundanstrichmaterial oder ein Finish-Material für Baumaterialien, ein Klebstoff, ein druckempfindlicher Klebstoff, ein Verarbeitungsmittel für Papier oder ein Finish-Material für Textilgewebe ist.

17. Wässrige Emulsion eines silikonmodifizierten Acrylatpolymers nach Anspruch 16, welche eine Farbe oder ein Finish-Material für Baumaterialien ist.

Revendications

1. Une émulsion aqueuse de polymère d'acrylate modifié par silicone qui est une émulsion de polymère d'acrylate préparée en soumettant un système (A) de monomère à une polymérisation en émulsion dans un milieu aqueux en la présence d'un émulsionnant (B), l'émulsion de polymère d'acrylate étant modifiée par silicone en utilisant un agent modifiant (C) contenant une structure de silicone pendant ou après la polymérisation en émulsion ; dans laquelle le système (A) de monomère comprend un monomère d'acrylate choisi dans le groupe consistant en un ester acrylique, un ester méthacrylique et leurs mélanges, le monomère d'acrylate contenant 5 % en poids ou plus par rapport au poids du système (A) de monomère, d'un ester cycloalcoylique ayant de 5 à 12 atomes de carbone dans la partie cycloalcoyle de l'acide méthacrylique ou leurs mélanges ; dans laquelle l'émulsionnant (B) est choisi dans le groupe consistant en un monomère à insaturation éthylénique contenant un groupe acide sulfonique, un monomère à insaturation éthylénique contenant un groupe sulfonate et

leurs mélanges ; et
 dans laquelle l'agent (C) modifiant contenant une structure de silicone comprend au moins un silane (I) contenant une structure de silicone représentée par la formule :



dans laquelle R^1 représente un atome d'hydrogène, un groupe hydrocarboné aliphatique ayant de 1 à 16 atomes de carbone, un groupe aryle ayant de 5 à 10 atomes de carbone, un groupe cycloalcoyle ayant 5 ou 6 atomes de carbone, un groupe vinyle, un groupe acrylique alcoyle ayant de 1 à 10 atomes de carbone dans la partie alcoyle ou un groupe méthacrylique alcoyle ayant de 1 à 10 atomes de carbone dans la partie alcoyle, et chaque R^2 représente indépendamment un groupe alcoxy ayant de 1 à 8 atomes de carbone, un groupe acétoxy ou un groupe hydroxyle, et au moins un élément choisi dans le groupe consistant en un silane cyclique et un silane (III) représenté par la formule :



dans laquelle chaque R^3 représente indépendamment un atome d'hydrogène, un groupe hydrocarboné aliphatique ayant de 1 à 16 atomes de carbone, un groupe aryle ayant de 5 à 10 atomes, un groupe cycloalcoyle ayant 5 ou 6 atomes de carbone, un groupe vinyle, un groupe acrylique alcoyle ayant de 1 à 10 atomes de carbone dans la partie alcoyle, un groupe méthacrylique alcoyle ayant de 1 à 10 atomes de carbone dans la partie alcoyle, et chaque R^4 représente indépendamment un groupe alcoxy ayant de 1 à 8 atomes de carbone, un groupe acétoxy ou un groupe hydroxyle ; et dans laquelle le rapport molaire du silane (I) au dit au moins un élément choisi dans le groupe consistant en un silane cyclique et un silane (III) est au moins de 10/100.

2. L'émulsion aqueuse de polymère acrylate modifié par silicone suivant la revendication 1, dans laquelle le système (A) de monomère et l'émulsionnant (B) sont respectivement utilisés en une quantité représentant de 80 à 99,95 % et en une quantité de 0,5 à 20 % du poids total du système (A) de monomère et de l'émulsionnant (B), et l'agent (C) modifiant contenant une structure de silicone est utilisé en une quantité qui satisfait les relations suivantes :

$$\frac{1}{2} \leq \frac{(A) + (B)}{(C)} \leq \frac{99}{1}$$

dans lesquelles (A), (B) et (C) représentent respectivement des quantités du système (A) de monomère, de l'émulsionnant (B) et de l'agent (C) modifiant en pourcentages en poids par rapport au poids total des substances (A), (B) et (C).

3. L'émulsion aqueuse de polymère acrylate modifié par silicone suivant la revendication 1 ou 2, dans laquelle le rapport du poids total du système (A) de monomère de l'émulsionnant (B) et de l'agent (C) modifiant au poids du milieu aqueux est de 75/25 ou inférieur à cette valeur.
4. L'émulsion aqueuse de polymère acrylate modifié par silicone suivant la revendication 1, dans laquelle le système (A) de monomère comprend en outre un comonomère pouvant être copolymérisé avec le monomère d'acrylate, le comonomère étant au moins un élément choisi dans le groupe consistant en un monomère d'acrylamide, un monomère de méthacrylamide, un monomère de vinyle et un monomère à insaturation éthylénique contenant un groupe acide carboxylique, et dans laquelle le monomère d'acrylate et le comonomère sont présents respectivement en une quantité représentant de 90 à moins de 100 % et en une quantité de 10 % ou moins du poids total du monomère d'acrylate et du comonomère.
5. L'émulsion aqueuse de polymère acrylate modifié par silicone suivant la revendication 4, dans laquelle le comonomère du système (A) de monomère est un monomère à insaturation éthylénique contenant un groupe acide carboxylique.
6. L'émulsion aqueuse de polymère acrylate modifié par silicone suivant la revendication 5, dans laquelle le monomère à insaturation éthylénique contenant un groupe acide carboxylique est au moins un élément choisi dans le groupe consistant en l'acide acrylique, l'acide méthacrylique, l'acide itaconique et son héli-ester, l'acide fumarique

et son héli-ester et l'acide maléique et son héli-ester.

7. L'émulsion aqueuse de polymère acrylate modifié par silicone suivant la revendication 1, dans laquelle le monomère à insaturation éthylénique contenant le groupe acide sulfonique ou le monomère à insaturation éthylénique contenant le groupe sulfonate de l'émulsionnant (B) est un composé à double liaison (polymérisé par voie radicalaire) et ayant un groupe acide sulfonique ou l'un de ses sels d'ammonium ou d'un métal alcalin.
8. L'émulsion aqueuse de polymère acrylate modifié par silicone suivant la revendication 7, dans laquelle le monomère à insaturation éthylénique contenant le groupe acide sulfonique ou le monomère à insaturation éthylénique contenant le groupe sulfonate de l'émulsionnant (B) est un composé à double liaison qui peut être polymérisé par voie radicalaire et qui a un substituant choisi dans le groupe consistant en un groupe alcoyle ayant de 1 à 20 atomes de carbone, un groupe alcoylétheroxyde ayant de 2 à 4 atomes de carbone, un groupe aryle ayant 6 ou 10 atomes de carbone et un groupe acide succinique, chacun d'entre eux étant substitué par un groupe acide sulfonique qui est sous la forme de l'un de ses sels d'ammonium, de sodium ou de potassium ou un composé vinylsulfonate ayant un groupe vinyle lié à un groupe acide sulfonique qui est sous la forme de l'un de ses sels d'ammonium, de sodium ou de potassium.
9. L'émulsion aqueuse de polymère acrylate modifié par silicone suivant la revendication 1, dans laquelle l'agent (C) modifiant contenant une structure de silicone comprend en outre au moins un élément choisi dans le groupe consistant en un siloxane linéaire contenant un groupe hydrolysable et un silane (II) représenté par la formule :



- dans laquelle chaque R^3 représente indépendamment un atome d'hydrogène, un groupe hydrocarboné aliphatique ayant de 1 à 16 atomes de carbone, un groupe aryle ayant de 5 à 10 atomes de carbone, un groupe cycloalcoyle ayant 5 ou 6 atomes de carbone, un groupe vinyle, un groupe acrylique alcoyle ayant de 1 à 10 atomes de carbone dans la partie alcoyle ou un groupe méthacrylique alcoyle ayant de 1 à 10 atomes de carbone dans la partie alcoyle, chaque R^4 représentant indépendamment un groupe alcoxy ayant de 1 à 8 atomes de carbone, un groupe acétoxy ou un groupe hydroxyle, et n est 0 ou 3 ; et le rapport molaire du silane (I) au total du au moins un élément choisi dans le groupe consistant en le silane cyclique et le silane (III) et du au moins un élément choisi dans le groupe consistant en un siloxane linéaire contenant un groupe hydrolysable et le silane (II) étant au moins de 10/100.
10. L'émulsion aqueuse de polymère acrylate modifié par silicone suivant la revendication 1, dans laquelle l'agent (C) modifiant est ajouté à un système de ladite polymérisation en émulsion de manière à ce que la modification par silicone de l'émulsion s'effectue pendant la polymérisation en émulsion.
 11. L'émulsion aqueuse de polymère acrylate modifié par silicone suivant la revendication 1, dans laquelle le système (A) de monomère comprend des systèmes (A^1) et (A^2) de monomère, comprenant chacun le monomère d'acrylate et l'émulsionnant (B) comprend des émulsionnants (B^1) et (B^2) choisis chacun dans le groupe consistant en le monomère à insaturation éthylénique contenant le groupe acide sulfonique, le monomère à insaturation éthylénique contenant le groupe sulfonate et leurs mélanges sous réserve que les systèmes (A^1) et (A^2) de monomère soient identiques ou différents, et que les émulsionnants (B^1) et (B^2) soient identiques ou différents, et dans laquelle on effectue la polymérisation en émulsion dans une séquence de stade (1) et de stade (2), dans laquelle, au stade (1), le système (A^1) de monomère est soumis à une polymérisation en émulsion dans un milieu aqueux en la présence de l'émulsionnant (B^1) pour obtenir ainsi une émulsion aqueuse préliminaire de polymère d'acrylate ayant un latex germe dispersé en son sein, et, au stade (2), le système (A^2) de monomère et l'émulsionnant (B^2), éventuellement avec un milieu aqueux, sont ajoutés à l'émulsion aqueuse préliminaire de polymère d'acrylate pour en effectuer une polymérisation en émulsion en produisant ainsi une émulsion aqueuse finale de polymère d'acrylate, la modification par silicone étant effectuée en utilisant l'agent (C) modifiant contenant une structure de silicone pendant ou après la polymérisation en émulsion.
 12. L'émulsion aqueuse de polymère acrylate modifié par silicone suivant la revendication 11, dans laquelle l'agent (C) modifiant est ajouté au stade (2) pour effectuer la modification par silicone pendant la polymérisation en émulsion.

13. L'émulsion aqueuse de polymère acrylate modifié par silicone suivant la revendication 11, dans laquelle l'émulsion aqueuse finale d'acrylate a été traitée par l'agent (C) modifiant pour effectuer la modification par silicone après la polymérisation en émulsion.

5 14. L'émulsion aqueuse de polymère acrylate modifié par silicone suivant la revendication 11, dans laquelle au stade (1) le système (A¹) de monomère et l'émulsifiant (B¹) sont utilisés respectivement en une quantité représentant de 80 à 99,95 % et en une quantité représentant de 20 à 0,05 % du poids total du système (A¹) de monomère et de l'émulsifiant (B¹) ; et au stade (2), le système (A²) de monomère et l'émulsifiant (B²) sont utilisés respectivement en une quantité représentant de 80 à 99,95 % et en une quantité représentant de 20 à 0,05 % du poids
10 total du système (A²) de monomère et de l'émulsifiant (B²), dans laquelle l'agent (C) modifiant comprenant une structure de silicone est utilisé en une quantité qui satisfait aux relations suivantes :

$$15 \quad \frac{1}{2} \leq \frac{(A^1) + (A^2) + (B^1) + (B^2)}{(C)} \leq \frac{99}{1}$$

dans lesquelles (A¹), (A²), (B¹), (B²) et (C) représentent respectivement des quantités du système (A¹) de monomère, du système (A²) de monomère, de l'émulsifiant (B¹), de l'émulsifiant (B²) et de l'agent (C) modifiant en
20 pourcentages du poids total des substances (A¹), (A²), (B¹), (B²) et (C); et dans laquelle le rapport du poids total du système (A¹) de monomère et de l'émulsifiant (B¹) au poids total du système (A²) de monomère et de l'émulsifiant (B²) est compris entre 1/99 et 99/1.

25 15. L'émulsion aqueuse de polymère acrylate modifié par silicone suivant la revendication 14, dans laquelle au stade (1) le système (A¹) de monomère contient de 0,5 à 30 % en poids d'un monomère à insaturation éthylénique contenant un groupe acide carboxylique par rapport au poids du système (A¹) de monomère.

30 16. L'émulsion aqueuse de polymère acrylate modifié par silicone suivant l'une quelconque des revendications 1 à 15, qui est une peinture, une sous-couche ou un revêtement de finition pour des matériaux de construction, un adhésif, un adhésif sensible à la pression, un agent de traitement des papiers ou une matière d'apprêt pour des tissus textiles.

35 17. L'émulsion aqueuse de polymère acrylate modifié par silicone suivant la revendication 16, qui est une peinture ou un revêtement de finition pour des matériaux de construction.